
2.3. Calibration and quantification

The following section details the basis for the quantitative capability of the instrument. The signal data acquired by the instrument can be directly converted to measured ion rates, and these to particulate mass. Similarly, the particle times of flight can be equated to particle vacuum aerodynamic diameters. However, several calibrations and supporting measurements must also be performed in order to be able to make these calculations. These were originally detailed by *Jayne et al.* [2000] and *Jimenez et al.* [2003a].

2.3.1. Ion rates

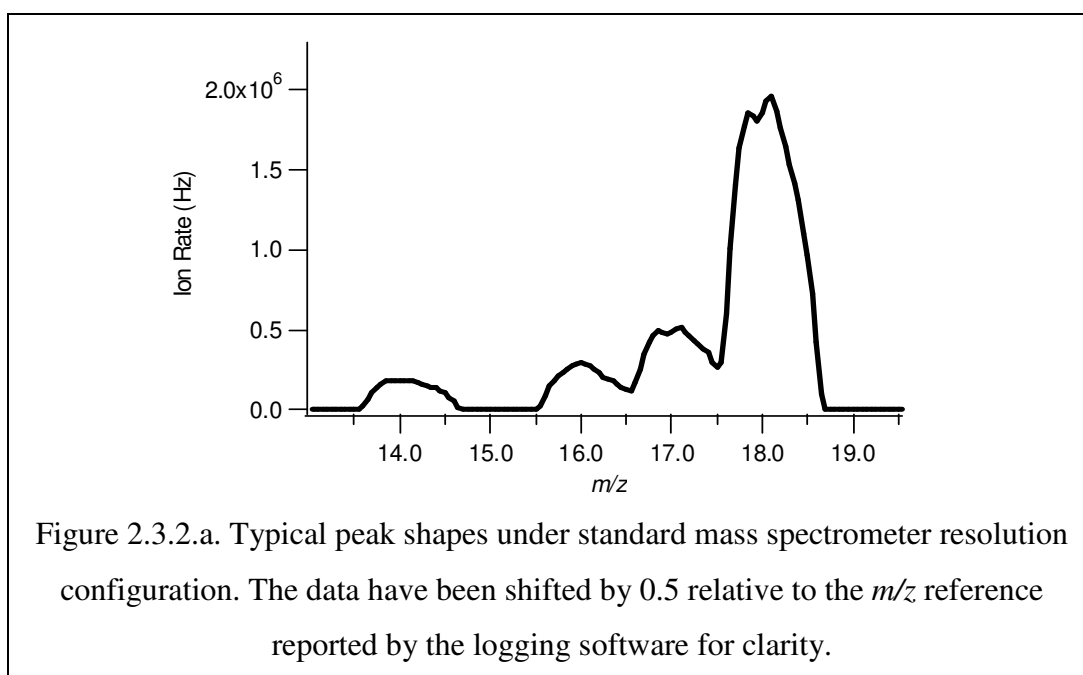
The primary data acquired by the logging computer are the voltage outputs from the preamplifier, which are proportional to the electrical current outputs of the electron multiplier. The latter are converted to detected ion rates (in Hz) by dividing by the average single ion signal strength (in V s). This quantity is dependent on the gains of both the preamplifier and the multiplier and is measured as part of the calibration protocol. To do this, the aerosol beam is blocked and the ionizer filament current reduced, so that individual ions, created from the background gas phase material, can be distinguished as pulses in the voltage time series that are numerically integrated and averaged.

This calibration is performed daily during continuous operation. During use, the efficiency of the amplification chain in the electron multiplier slowly degrades, so the voltage applied has to be periodically increased in order to keep the multiplier gain approximately at the desired gain (around 3×10^6). The voltage must be carefully set during each calibration; if the gain is too low, the ions detected during the calibration may not produce enough signal to be sufficiently greater than the threshold voltage imposed by the amount of electronic noise present. This results in the smaller of the single ion pulses being systematically ignored and an erroneous average single ion strength being derived. If the multiplier voltage is set too high, some of the stronger signals measured during data acquisition may give preamp output voltages higher than the maximum measurable by the data acquisition system (5 V). Also, when operated at a higher voltage, the multiplier tends to deteriorate faster. The multiplier is replaced when the voltage required exceeds 3 kV or it starts outputting current in the absence of ions (known as a dark current). Often, a partly aged multiplier is replaced at the

beginning of a measurement campaign regardless, to reduce the chance that it will have to be replaced mid-campaign, as this typically results in at least a day's downtime and an unwanted increase in background pressure.

2.3.2. Mass

An important feature of the AMS is the ability to equate an ion rate detected in the mass spectrometer to a mass concentration of a given chemical species in a sample. However, the mass spectrum must first be converted into discrete values for individual m/z 's in order to be interpreted. The quadrupole is configured so that during scanning, signals due to specific ions form distinct peaks in a mass spectrum with well-defined flat tops. Peaks of this shape indicate that within the plateaux, maximum ion transmission is being achieved (within the capabilities of the quadrupole) while not interfering with adjacent m/z (figure 2.3.2.a). The plateaux in the mass spectra have m/z widths of approximately 0.45 and the averaged height is taken to be the detected ion rate for that m/z .



To convert an ion rate signal I , in detected ions per second or Hz, to an ambient mass loading C , in $\mu\text{g m}^{-3}$, the following generalized formula is applied, following *Jimenez et al.* [2003a].

$$C = 10^{12} \cdot \frac{MW}{IEQN_A} I, \quad (2.3.2.i)$$

where MW is the relative molecular weight of the parent species in g mol^{-1} , N_A is Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$), Q is the volumetric flow rate into the

instrument in $\text{cm}^3 \text{s}^{-1}$ and IE is the ionization efficiency, a dimensionless quantity equalling the ratio of ions detected by the multiplier to the number of available desorbed molecules of the parent chemical species in the detection region. Note that the IE depends on the probability of producing a positively charged ion from a vapour molecule, the transmission efficiency of the ions passing through the quadrupole and the detection efficiency of the electron multiplier. The factor of 10^{12} is included to make the conversion from g cm^{-3} to $\mu\text{g m}^{-3}$.

The ionization efficiency of nitrate, IE_{NO_3} , is determined during routine calibration, as described by *Jayne et al.* [2000]. Ammonium nitrate particles are generated from an aqueous solution using a nebuliser or collision atomizer and size selected using a DMA. By applying the density of ammonium nitrate (1.725 g cm^{-3}) and a measured shape factor of 0.8 to the spherical volume associated with the mobility diameter selected (normally 350 nm, so that individual particles have enough mass to be reliably distinguished and counted), the average mass of the singly charged particles is calculated. This is then compared to the average integrated signal pulse produced by single particles in the instrument to calculate the ionization efficiency. Multiply charged particles are eliminated from this calibration analysis by running the instrument in TOF mode and ignoring particles with a time of flight greater than a threshold value, i.e. with too large an vacuum aerodynamic diameter. Additionally, the strength of the solution (normally $0.015 - 0.05 \text{ mol dm}^{-3}$) is chosen to result in more dry particles of the desired size being produced compared to the multiply charged sizes, but this is dependent on the aerosol generation system.

The signal strengths of the MS and TOF modes are also compared and checked for consistency to ensure the instrument is configured and working correctly. The number of particles counted by the AMS is also compared with a CPC to verify optimum collection efficiency. This calibration is normally performed once every two to five days or so during continuous ambient sampling or once per day or more for laboratory experiments.

2.3.3. Particle size

2.3.3.1. Aerodynamic sizing

The aerodynamic diameter of a particle for a given sizing method is defined as the diameter of a sphere of unit density (1 g cm^{-3}) that would behave the same as the subject particle during sizing. In this case, the particle acceleration responsible for the

sizing mainly occurs at the nozzle, where drag forces accelerate the particles during the supersonic gas expansion. Large, heavy particles reach smaller speeds due to their higher inertia, while non-spherical particles will reach relatively higher speeds due to the increased drag force. Therefore, the aerodynamic diameter of a particle in this instrument will be dependent on its geometric size, its shape and its density. Well-established instruments that measure particle sizes aerodynamically, such as cascade impactors and APSs, relate their measured aerodynamic diameters (D_a) to particle volume-equivalent diameters (D_v) by the square root of the particle densities ($\rho_p^{1/2}$) [McMurry *et al.*, 2002]. The AMS, however, sizes particles at a much lower pressure, where the particle diameters are much lower than the mean free path of the gas molecules (the free-molecular regime), so instead, the aerodynamic diameters of particles are now proportional to the densities (ρ_p), as described by the following equation, taken from Jimenez *et al.* [2003b; 2003c].

$$D_{va} = \frac{\rho_p}{\rho_0} \chi_{v,inv} D_v \quad (2.3.3.1.i)$$

Because of the difference in the definitions of the two aerodynamic diameters, the aerodynamic diameter measured by the AMS in the free-molecular regime is referred to as the ‘vacuum aerodynamic diameter’ (D_{va}) to distinguish it from the continuum/transition regime or ‘classical’ aerodynamic diameter. ρ_0 is the unity density of 1 g cm^{-3} and $\chi_{v,inv}$ is a dimensionless shape factor that equals the ratio of the drag force experienced by a volume-equivalent sphere to that experienced by the particle. A similar shape factor (S) was defined by Jayne *et al.* [2000], although this is used to relate a particle’s vacuum aerodynamic diameter to its electromobility diameter (D_m), as follows:

$$D_{va} = \frac{\rho_p}{\rho_0} S D_m \quad (2.3.3.1.ii)$$

It must be noted that these shape factors are numerically different, as a particle’s electromobility diameter is also dependent on particle shape. The product of a particle’s relative density and shape factor is sometimes referred to as the ‘effective density’ or ρ_{eff} .

2.3.3.2. Size calibration

A velocity calibration is routinely performed at least once per deployment, as described in Jayne *et al.* [2000]. Particles of known sizes are introduced into the

instrument and their times of flight measured. Polystyrene latex (PSL) spheres are normally used (e.g. Duke Scientific Corporation Nanosphere 3000 series, Palo Alto, CA, USA) as these can be purchased with specific and traceable diameters, are spherical and have a density close to unity (1.05 g cm^{-3}), making the calculations much easier and much less prone to uncertainties. As the PSL is less volatile than other chemicals normally vaporised by the instrument, the oven temperature must be increased to at least $800 \text{ }^\circ\text{C}$ to ensure rapid vaporisation and adequate particle sizing. Ammonium nitrate particles, selected using a DMA, are often used to verify a calibration.

The particle velocities in the AMS (v_p), in m s^{-1} , are calculated from the times of flight (t_p), in s and the chamber length (L_c), in m and are plotted against their calculated vacuum aerodynamic diameters and the following function is fitted to the points, using a non-linear least squares fit.

$$v_p = \frac{L_c}{t_p} = \frac{v_g - v_l}{1 + (D_{va}/D^*)^b} + v_l, \quad (2.3.3.2.i)$$

where D_{va} is the particle vacuum aerodynamic diameter in nm, v_g the gas velocity on exiting the nozzle in m s^{-1} , v_l the gas velocity within the aerodynamic lens, prior to the nozzle expansion, in m s^{-1} , and D^* (in nm) and b (dimensionless) are calibration constants. The function is a version of that presented by *Jayne et al.* [2000], modified to include the v_l parameter [*Jimenez*, In preparation]. Once values have been assigned to v_g , v_l , D^* and b , the equation can be reversed to convert particle times of flight to vacuum aerodynamic diameters.

It is desirable to fit all four variables independently (which has been done for all the results presented in this thesis), although if there are not enough data points, it is possible to estimate v_g from the measured time of flight of the gas phase signal and v_l from the lens pressure, geometry and flow rate, which can help constrain the fit. However, it is very hard to definitively estimate the ‘true’ values of these parameters. For instance, the different gases have different velocities upon leaving the nozzle, leading so different values of v_g , depending on which m/z is measured. Also, as the gas undergoes several rapid accelerations and decelerations in the lens, assigning one definitive velocity is difficult.

While there is some debate over which is the better method of fitting, it must be remembered that v_g and v_l represent the asymptotes of the size-dependent particle velocities ($D_{va} = 0$ and ∞ respectively), so if the calibration particles cover the range of

sizes of the particles encountered during measurement and the fitting function adequately reflects the calibration data, the specific values of v_g and v_l used are not important for the pure purpose of data inversion. However, if the range of the calibration data points does not cover all the sizes expected, it means that the calibration curve must be extrapolated and the values of v_g and v_l do become important for the sizing of very small and very large particles respectively.