Chapter Three: The Aerodyne Aerosol Mass Spectrometer (AMS)

3.1 AMS description

The Aerodyne aerosol mass spectrometer (AMS) design is based on earlier efforts to perform on-line, quantitative particle mass spectrometric measurements using a heated surface for particle vaporisation immediately followed by standard 70 eV electron impact ionisation and subsequent ion analysis using a quadrupole mass spectrometer [*Allen and Gould, 1981; Sinha and Friedlander, 1985*]. The AMS, Figure 3.1, draws particles into vacuum through a unique aerodynamic lens sampling inlet system [*Liu et al., 1995a; Liu et al., 1995b; Zhang et al., 2002*], which focuses aerosol particles into a narrow, collimated beam that impacts on a porous tungsten surface (the vaporiser) heated typically to 500 ^{o}C under high vacuum (~ 10^{-8} torr). The non-refractory fraction of the particles, mostly the volatile and semi-volatile components, flash vaporise upon contact with the vaporiser surface on a time scale of a few microseconds, and the resultant gaseous molecular constituents are then ionised using a 70 eV electron impact ionisation source positioned such that the maximum electron density and the centre of the vaporised plume are co-located in the extraction zone of the mass spectrometer. A quadrupole mass spectrometer (QMA 410, Balzers Instruments, Balzers, Liechtenstein) is utilised to analyse the positive ions with unit mass-to-charge (*m/z*) resolution. This chapter describes the individual components of the AMS, its principles, calibrations and modes of operation, and how it can provide quantitative measurements of the chemical composition and size distribution of submicron aerosol particles.

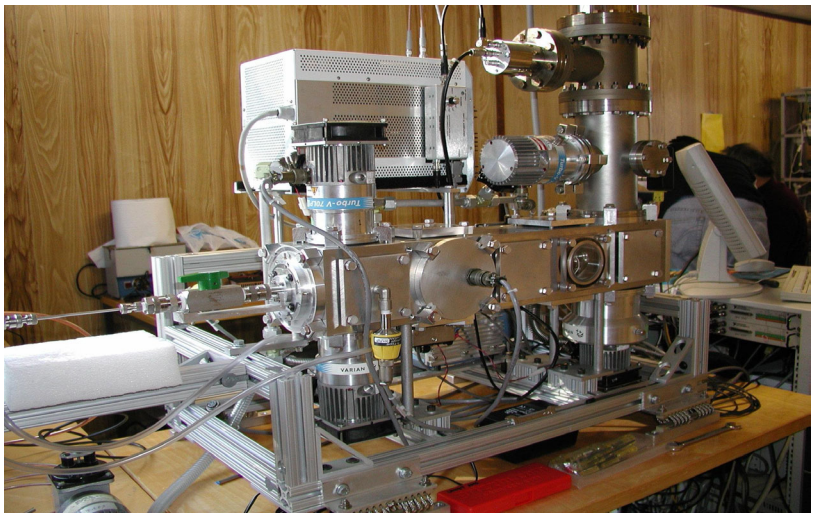

Figure 3.1: A picture of the Aerodyne aerosol mass spectrometer (AMS)

The instrument consists of three differentially pumped chambers: an aerosol sampling chamber, a particle-sizing chamber, and a particle detection and chemical analysis chamber, separated by a skimmer and a channel aperture respectively. All AMS components will be described in detail in this section. A basic schematic of the AMS is shown in Figure 3.2. The original AMS power and weight specifications, produced by Aerodyne Inc., are listed in Table 3.1.

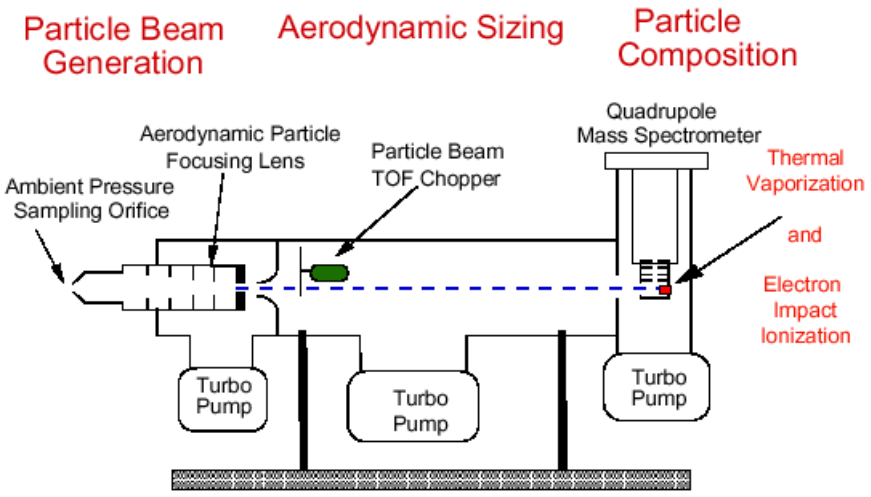

Figure 3.2: Schematic diagram of the Aerosol Mass Spectrometer (AMS)

System	Amps	Volts	Watts	Weight (pounds)
Vacuum Chamber				96.5
5-Turbo Pumps under load	7.2	24	172.8	
5-Cooling Fans	0.625	24	15	
Backing Pump	2	24	48	18
Detection				
Quadrupole mass spectrometer				28
Ioniser controller	0.9	115	103.5	26
RF Box				11.5
Rack Mount Boxes (w/cables)				
Turbo pump Control Box				11.5
Chopper/Vaporiser/EM Supply	2	24	48	7.5
AC/DC 24 V supply				9.5
SenTorr Pressure Gauge Controller	0.1	115	11.5	6
Data Acquisition				
Rack Mount Computer	0.6	115	69	29
		Total	**467.8**	**243.5**
	Design Goals		**< 1000**	**< 330**

Table 3.1: AMS power and weight specifications, 25.5" Long Chamber (Aerodyne Research Inc., 2000)

3.1.1 Aerosol sampling chamber

Aerosol particles are sampled through a 100 μm or 120 μm critical orifice at a flow rate of 1.5 or 2 cm^3 s^{-1}, respectively. Particles are then accelerated through an aerodynamic lens similar to that designed and verified by *Liu et al.*, [*1995a; 1995b*]. The chamber pressure is maintained below 10^{-3} torr using two Varian 70 l s^{-1} turbo molecular pumps. The aerodynamic lens (Figure 3.3) consists of a cylindrical barrel (1 cm diameter, 30 cm long), which contains a series of five circular apertures of sequentially decreasing diameter (5 mm id to 3 mm id) that is used to focus particles into a narrow collimated beam before accelerating them, supersonically, through a nozzle. The addition of a set of lenses to the barrel leads to a periodic series of contractions and expansions in the air streamlines. However, because of their inertia relative to the gas molecules, particles follow trajectories that deviate from the gas streamlines in the lens. Those with enough inertia will be carried across the gas streamlines onto the axis of the barrel and remain focused on-axis as they expand through the nozzle into vacuum, producing a narrow, low-divergence particle beam as illustrated in Figure 3.4 [*Liu et al., 1995a; Liu et al., 1995b; Ziemann, 1998*].

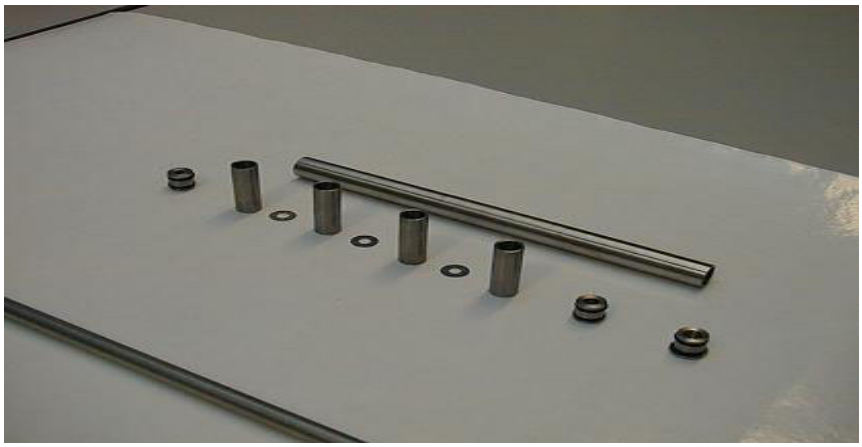

Figure 3.3: A picture of the components of the aerodynamic lens system

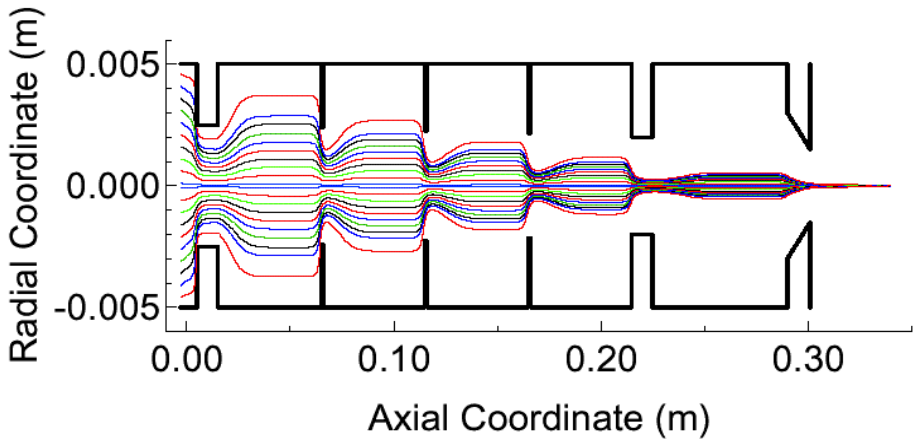

Figure 3.4: FLUENT simulation results illustrating the focusing action of the aerodynamic lens for 100 nm diameter spheres (Jayne et al., 2000)

Jayne et al., [*2000*] have numerically modelled, using a commercially available fluid dynamics program (FLUENT), and experimentally verified the performance of the aerodynamic lens used in the AMS. Calculations describing the particle size-dependent transmission efficiency and particle velocities were performed and were found to support the results of the measured lens performance as shown in Figure 3.5. It was shown that spherical particles in the size range of about 70 to 650 nm were transmitted with 100% efficiency using a 100 μm pinhole, allowing for most of the accumulation mode aerosol to be analysed. Subsequent modifications to the lens system improved the lower cut-off of lens transmission efficiency down to 30 nm [*Zhang et al., 2002*]. This change did not adversely affect the transmission of the larger particles, as the high diameter cut-off in the lens design is dictated by the critical orifice used to control the flow. Particles smaller than the lower cut-off of the lens have too little inertia to be focused and the majority of them follow the gas streamlines and are not collimated into the beam. Particles larger than the upper limit are mostly lost through impaction on the critical orifice or on the first lens stage, resulting in a gradual decrease in the transmission efficiency with increasing particle diameter above the upper limit size.

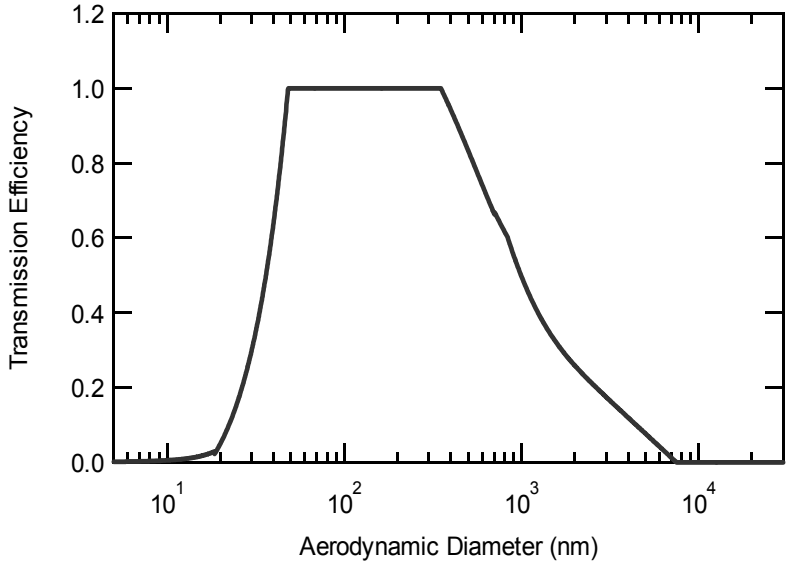

Figure 3.5: Aerodynamic lens transmission efficiency as a function of particle size (Jayne et al., 2000)

Brownian motion and lift forces on particles during nozzle expansion determine the minimum width of particle beams produced using an aerodynamic lens system [*Liu et al., 1995a; Liu et al., 1995b*]. Brownian motion is caused by the random collisions of air molecules with the particles and causes the particles to agitate about the axis as they accelerate through the nozzle. This affects all particles, causing the particle beam to diverge and leads to a radial broadening of the beam profile. Lift force only affects non-spherical particles during nozzle acceleration and leads to beam broadening. It is usually difficult to formulate the lift force on an arbitrarily shaped particle, because it depends on the particle's geometry and orientation. The overall effect causes a reduction in the aerodynamic lens' transmission efficiency of non-spherical particles.

3.1.2 Particle sizing chamber

The aerodynamic lens is aligned so that the focused particles are accelerated into a particle-sizing chamber through a 2 mm diameter skimmer cone, which helps to remove some of the gases and improve the vacuum. The particle-sizing chamber is a 39.5 cm long flight tube maintained at 10^{-5} torr by another 70 l s^{-1} Varian turbo molecular pump. The supersonic expansion of the particle-laden air on exiting the aerodynamic lens creates a size-dependent particle velocity distribution, where small particles travel faster

than larger ones. Particle velocity can be determined by measuring the particle time-of-flight over a known distance. A calibration curve, relating particle velocity to its vacuum aerodynamic diameter (defined below) can then be used to determine vacuum aerodynamic diameters for measured particles as will be described in section 3.4.3. A mechanical, rotating chopper disc (5 cm diameter) with two radial slits, positioned 180 degrees apart, is coupled to an optical sensor to define the start of the particle TOF cycle and is used to synchronise time-resolved particle detection. The TOF measurement relies on fast particle vaporisation and detection (of the order of microseconds) that provides the end of the time of flight cycles. The chopper operates at a fixed frequency, typically in the range of 100 to 150 Hz, defining a TOF cycle of 10 ms or less. The chopper also has a fixed duty cycle, typically 2 - 3.5%, which determines the aerosol throughput from the lens to the detector. The chopper duty cycle is determined by the width and relative position of the slits, and also the diameter of the chopper wheel. A servo motor is used to control the chopper position, relative to the aerosol particle beam, according to the AMS mode of operation as will be discussed in section 3.2.

The AMS measures vacuum aerodynamic diameter since the particle time of flight is measured in a free-molecular regime flow, unlike the classical aerodynamic diameter that is measured in a continuum regime flow. The mean free path at the operational pressure of an instrument determines the regime flow type. The difference between vacuum and classical aerodynamic diameters are discussed in detail elsewhere [*Jimenez et al., 2003a*], and the following expression have been used to describe their relationship:

$$D_{va} = \frac{\rho_p}{\rho_0} \cdot \frac{D_v}{\chi_v} \tag{3.1}$$

where D_{va} is the vacuum aerodynamic diameter, χ_v is the dynamic shape factor in the free-molecular regime, D_v is the classical volume-equivalent diameter, ρ_p is the density of the particle material and ρ_0 is the unit density (1 g cm^{-3}).

3.1.3 Particle detection and chemical analysis chamber

The particle detection chamber is separated from the particle-sizing chamber by a 4 mm diameter aperture, and is pumped by another Varian 70 l s^{-1} turbo molecular pump. It contains a cylindrical sub-chamber separated by a 1 mm aperture, which contains the vaporisation and ionisation cell and the quadrupole mass spectrometer and is pumped by a Varian 250 l s^{-1} turbo molecular pump. This configuration of differentially pumped chambers allows for the pressure in the detection chamber to be as low as 10^{-8} torr. Particle detection is carried out by directing the focused aerosol particle beam into a vaporisation and ionisation cell, which is coupled to a quadrupole mass spectrometer (QMS) as illustrated in Figure 3.6. The particle beam impacts on a tungsten surface typically heated to ~ 500 ^{o}C (the vaporiser) causing the non-refractory fraction of the aerosol particles to flash vaporise. The term "non-refractory" is defined operationally as those species that evaporate at the vaporiser temperature and vacuum conditions. The vaporiser is heated by passing up to 5 watts of power through a 0.1 mm diameter coiled tungsten wire positioned inside the vaporiser body. An electron impact ionisation source (a tungsten filament emitting 70 eV electrons) is then used to ionise the formed gaseous molecular cloud. The resultant positive ions are focused into a quadrupole mass spectrometer and are separated according to their mass-to-charge (*m/z*) ratio. The ions are detected by electron multiplier (ETP model 1440, SGE Inc., Austin, TX, USA), which converts the ion current to an electronic current. A preamplifier is used to convert this current into voltage, which is sampled using National Instruments data acquisition boards on the controlling computer. The quadrupole mass spectrometer is the standard, commercial type available from Balzers Instruments (QMA 410, Balzers Instruments, Balzers, Liechtenstein) with the exception of the vaporiser. The fact that the vaporiser is made of a conducting metal means that it adversely affects the field geometries in the ionisation region. This is addressed by applying a suitable DC voltage to the vaporiser, namely the heater bias.

The separation of the particle vaporisation and ionisation steps is a very significant feature of the particle detection process, which makes the AMS a quantitative instrument. It allows the ionisation process to be performed on a gaseous molecular

cloud using a standard 70 eV electron source, which provides conditions that can maintain quantitative detection for multi-component particles [*Jayne et al., 2000*].

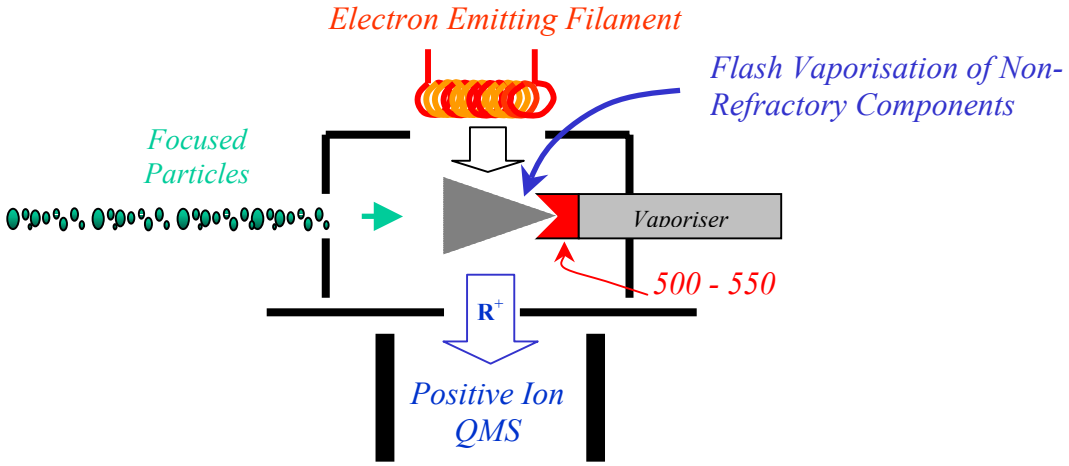

Figure 3.6: Particle vaporisation and ionisation cell

3.1.4 Other AMS components

The three turbo molecular pumps in the aerosol sampling and particle sizing chambers are backed by a diaphragm pump, while the rest of the turbo molecular pumps are configured in a sequence where the fourth pump is backed from the bleed valve of the third and the fifth is backed by the bleed valve of the fourth. All the relevant controlling electronics are housed in a separate rack, which accompanies the main AMS body. This includes the controllers for the turbo molecular pumps, the mass spectrometer, the vaporiser, the chopper, the electron multiplier detector and the preamplifier. A computer equipped with two National Instruments data acquisition boards is used to control the various AMS components using a data logging software program written in visual basic [*Jimenez et al., 2003b*].

3.2 Modes of operation

The AMS can produce two types of data: mass spectra of the species present in/on the particles, without size information; and mass-weighted size distributions as a function of the vacuum aerodynamic diameter ($dM/dlogD_{va}$) of the aerosol particles at a series of selected mass fragments (*m/z*) representing various chemical species. These types of

data are achieved by alternating, typically every few seconds, between two modes of operation; the mass spectrometer mode and the time-of-flight mode.

3.2.1 The mass spectrometer mode (MS)

In this mode of operation, the quadrupole mass spectrometer is scanned continuously from 1 to 300 *m/z*, at a rate of 1 *m/z* per millisecond, while aerosol particles are directly impacted onto the vaporiser. This provides an overall mass spectrum of the total ensemble of aerosol particles without any information on particle size. The position of the particle beam chopper is alternated every 5 seconds in such a way that it either blocks the aerosol beam completely and an average background mass spectrum is obtained (beam blocked position) or it fully moves out of the way of the aerosol beam and an average mass spectrum of all the detected particles is recorded (beam open position). The difference between the open and blocked spectra is a mass spectrum of the non-refractory, mostly volatile and semi-volatile, constituents of the particle ensemble. The resulting mass spectra can, in principle, be quantified and classified for different chemical species as will be discussed in sections 3.3 and 3.6, respectively. An example of a typical mass spectrum is displayed in Figure 3.7.

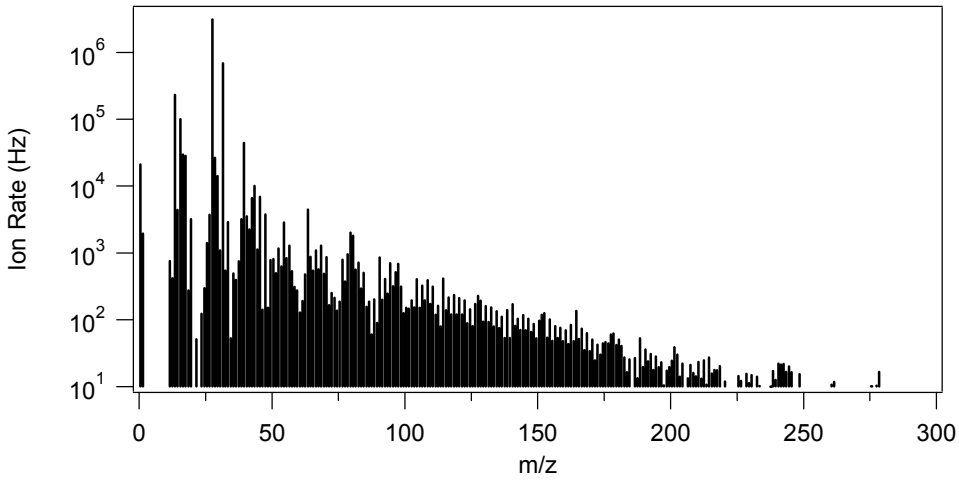

Figure 3.7: An example mass spectrum calculated from the difference between two spectra recorded in the 'open' and 'blocked' beam positions.

3.2.2 The Time-of-Flight mode (TOF)

This mode of operation is based on the fact that aerosol particles gain a velocity distribution as they accelerate from the aerodynamic lens into vacuum that is dependent

on their size, shape and density. The quadrupole mass spectrometer is set to detect one mass fragment (*m/z*) over several chopper cycles but is programmed to cycle through several selected mass-to-charge (*m/z*) settings at a 3 Hz rate. Typically the *m/z* settings are chosen so that they can be identified with specific chemical species. At the same time, the particle beam chopper is positioned in a way that allows pulses of aerosol particles and gas phase material through at regular intervals. As the disc of the chopper rotates, aerosol particles can only pass through when one of the chopper disc slits is in line with the particle beam. The chopper is typically operated at a rate of 100 to 150 Hz, allowing for a time-of-flight cycle of 10 ms or less. The control software can identify the times when aerosol particles are let through using an optical sensor located on the particle beam chopper assembly and data collection is synchronised to the trigger from the optical sensor. The time taken by a particle to travel from the chopper assembly until it is detected by the quadrupole mass spectrometer can be used to calculate its velocity, giving the known distance between both components. This method assumes that the time taken for ions to reach from the ionisation cell to the electron multiplier detector is negligible and has been shown to be the case for non-refractory aerosol [*Jayne et al., 2000*]. Data obtained in this mode can be transformed into mass distributions of selected mass fragments as a function of their vacuum aerodynamic diameter after applying the appropriate calibrations, as will be discussed in section 3.4.3. The distributions produced in this mode of operation are normally offset from the zero line due to the signal produced by background gases. This offset can be determined by averaging the signal at regions of the distribution where aerosol particles should not exist. These regions are found at the beginning and end of the distribution and correspond to particle diameters that are too small or large to be expected.

The graphs in Figure 3.8 are examples of the types of data obtained by the TOF mode of operation. The top panel graph shows a *size-resolved number distribution* for a selected *m/z*. Typically, this distribution is biased towards larger particles (> 150 – 200 nm); as smaller particles produce signals that are buried in the background signal level and cannot be clearly distinguished by the analysis software. A particle detection threshold is normally determined by moving the chopper into the "beam blocked" position and registering the maximum signal produced by background material and electronic noise

at the selected mass fragments. During operation, if a signal greater than this threshold level is detected, it is interpreted and counted as a single particle. The graph in the bottom panel of Figure 3.8 illustrates an example of a *size-resolved mass distribution* of a selected *m/z*. Unlike the counted single particle distribution, the mass distribution (averaged over a few seconds or minutes) accounts for the mass of all particles at this *m/z* that make it to the electron multiplier detector as a function of D_{va}. The area of the mass distribution for a given chemical component is proportional to the total particle mass.

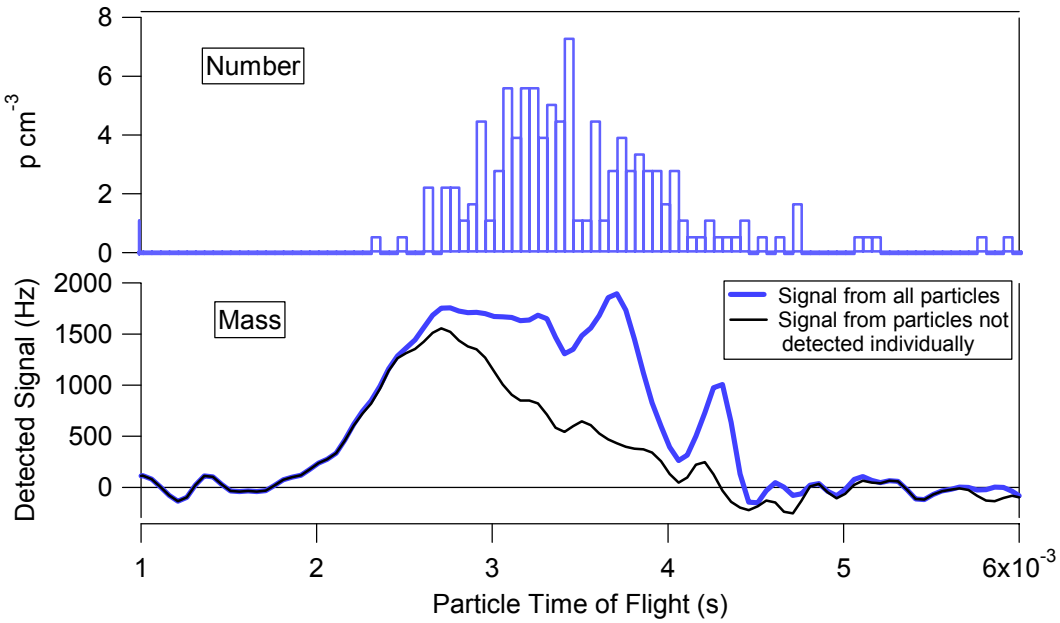

Figure 3.8: An example of the number and mass resolved size distribution data obtained during the TOF mode of operation of the AMS for m/z 43.

3.3 Theoretical basis of AMS quantitative measurements

One of the most important features of the AMS, compared to other aerosol mass spectrometry techniques, is the ability to equate the detected ion rate in the mass spectrometer to a mass concentration of a certain chemical species in the sampled aerosol particles. The data acquisition software receives the voltage outputs from the preamplifier, which are directly proportional to the electrical current outputs of the electron multiplier detector. The latter are divided by the average single ion signal strength in order to be converted to detected ion rates. The value of the single ion strength depends on the gains of both the electron multiplier and the preamplifier and is

measured during a regular calibration protocol, which is described in section 3.4.7. The raw data are recorded in a form of a continuous mass spectrum, which is converted into discrete m/z channels in order to be interpreted. This is achieved by setting the resolution of the quadrupole mass spectrometer so that peaks due to ion mass fragments, with well-defined flat tops, should not affect adjacent peaks. The widths of the plateaux are defined to 0.4 amu, and the averaged height is considered to be the detected ion rate for an *m/z*.

Jimenez et al., [*2003b*] adapted the following formula from *Bley* [*1988*] in order to convert an ion rate signal, *I*, to the equivalent mass concentration, *C in* $\mu g\ m^{-3}$:

$$C = \frac{1}{IE}\frac{1}{Q}\frac{MW}{N_A}I \tag{3.2}$$

where MW is the molecular weight of the parent species, N_A is Avogadro's number, Q is the volumetric flow rate into the AMS, and *IE* is the ionisation efficiency, a dimensionless quantity equalling the ratio of the number of ions detected by the electron multiplier to the number of available desorbed molecules of the parent chemical species. It is important to note that the *IE* depends both on the ionisation efficiency for producing charged ions and the transmission efficiency of the quadrupole mass spectrometer of those ions.

Molecules of most chemical species undergo fragmentation during electron impact ionisation, which results in various numbers of mass fragments (*m/z*) depending on the structure of the chemical species under study. For example, the nitrate group (NO_3^-) produces two major mass fragments in the mass spectrum of ammonium nitrate at *m/z* 30 and 46 arising from NO^+ and NO_2^+, respectively. To measure the total mass of nitrate, the formula above must be updated to account for both fragments as follow:

$$C_{NO_3} = \frac{1}{IE_{NO_3}}\frac{1}{Q}\frac{MW_{NO_3}}{N_A}\cdot\sum_{f=30,46} I_f \tag{3.3}$$

The ionisation efficiency of nitrate, IE_{NO3}, is measured during routine calibration, as described by *Jayne et al.*, [*2000*] and discussed in section 3.4.8.

The following correction, which is independent of chemical species, should be applied to all AMS data to account for varying instrument response for different *m/z* values.

$$I_{m/z}^{corrected} = \frac{I_{m/z}^{measured}}{T_{m/z} \cdot G_{m/z}} \tag{3.4}$$

where $I_{m/z}$ is the signal intensity as a function of *m/z*, $T_{m/z}$ is the relative transmission of the quadrupole mass spectrometer for a given *m/z* and $G_{m/z}$ is the relative gain and detection efficiency of the electron multiplier. This correction has not been applied to data presented in this thesis or all published AMS data, to date. The relative transmission of the quadrupole as a function of *m/z* has not yet been determined, though should be a minor correction according to the manufacturer [*Balzers Instruments, 2000*].

This method can be extended to calculate the mass concentration of other chemical species such as sulphate, ammonium or organics by summing the signals of the appropriate mass fragments (*m/z*) and relating the MW_s/IE_s ratio of this species to a measured *MW/IE* ratio of a calibration compound such as ammonium nitrate (NH_4NO_3). The assumption is that the ionisation cross section of the parent molecules is proportional to the number of electrons present. *Jimenez et al.*, [*2003b*] used the NIST data for electron impact ionisation cross sections (σ) with 70 eV electrons versus the number of electrons in the molecule (Figure 3.9) to illustrate the validity and limitations of this assumption. The ionisation efficiency of a molecule is directly proportional to σ since the latter represents the efficiency of ionisation of a per-molecule basis. The number of electrons in a molecule, N_e, is highly correlated with its molecular weight due to the fact that the ratio of atomic number to atomic weight is very similar for most of the atoms of the molecules found in atmospheric aerosol particles such as C, O, N and S. This leads to the assumption that since IE_s is directly proportional to σ, and N_e is approximately proportional to MW_s. IE_s/MW_s will be proportional to σ/N_e. It can be inferred from Figure 3.9 that IE_s/MW_s is approximately constant for molecules of a

given type, allowing for the following generalisation to be made about a chemical species, *s*, when compared to nitrate:

$$\frac{MW_S}{IE_S} = \frac{1}{K_C} \cdot \frac{MW_{NO_3}}{IE_{NO_3}} \tag{3.5}$$

where K_c is a dimensionless constant, specific to the chemical species type and can be determined experimentally. It has been found that K_c is equal to 1 for most inorganic species, approximately 2 for hydrocarbons, and 1.5 for oxidised organic compounds [*P. J. Silva, Aerodyne Research, Inc. unpublished laboratory data, 2002*].

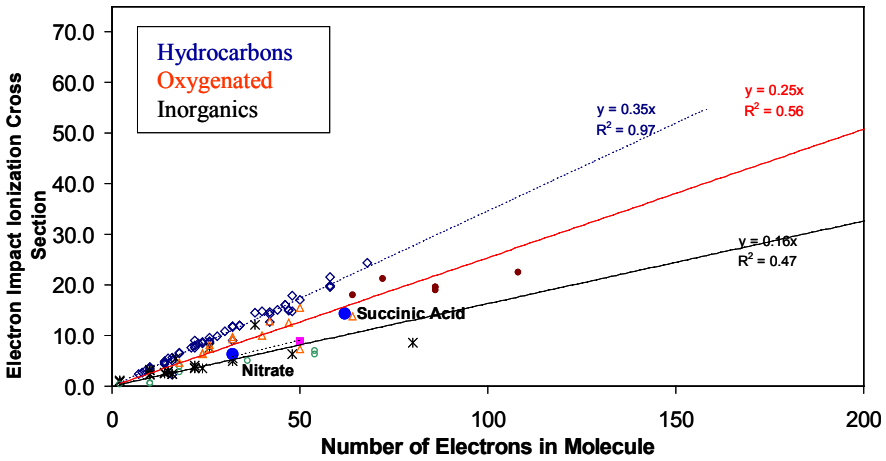

Figure 3.9: Electron impact ionisation cross section as a function of the number of electrons in a molecule for various inorganic and organic compounds (Jimenez et al., 2003b)

A generalised formula for the calculation of the mass concentration, in μg m^{-3}, for a particular chemical species, *s*, can be obtained by incorporating equations 3.4 and 3.5 into 3.3, as follow:

$$C_s = R_t \frac{\sum_f I_{sf}^{corr}}{N_A Q} \frac{MW_{NO_3}}{IE_{NO_3}} \tag{3.6}$$

where $\sum_f I_{sf}^{corr}$ is the total ion current (in ions s^{-1}) for all the mass fragments produced by a given species (*s*), MW_{NO3} is the molecular weight of nitrate (62 g mol^{-1}), IE_{NO3} is the

measured ionisation efficiency for nitrate, N_A is Avogadro's number and Q is the volumetric flow rate into the AMS. R_t is a response factor that takes into account the differences in ionisation efficiency per unit mass for different species with respect to the measured IE_{NO3}/MW_{NO3}. R_t is the inverse of the relative ionisation efficiency per unit mass for species s, RIE_s. In practice, the measured IE_{NO3} is determined only from the ion fragments 30 (NO^+) and 46 (NO_2^+) during calibration. Laboratory work has shown that these signals account for about 90% of the total nitrate ion signal for ammonium nitrate [*Hogrefe et al., 2004*]. Thus RIE_s also accounts for this difference between the true IE_{NO3} and the measured IE_{NO3}.

Equation 3.6 requires that the ion signals produced by a given species at all *m/z* peaks are known. In some experiments, however, the contribution of a species to certain peaks in the mass spectrum cannot be directly measured due to overwhelming interference from other ions detected at the same *m/z*, such as the S^+ peak (*m/z* 32) in the sulphate spectrum, which is dwarfed by the O_2^+ peak from gas phase oxygen when sampling in air. The AMS data analysis software package described by *Allan et al.*, [*2003b; 2004b*], and briefly described in section 3.6, attempts to account for the non-measurable *m/z* peaks for each species by using ratios derived from laboratory calibrations to estimate the peaks that cannot be measured (such as *m/z* 32 arising from the vaporisation/ ionisation of sulphate). Equation 3.6 can be rewritten as:

$$C_s = R_t C_s^{eq} \tag{3.7}$$

where C_s^{eq} is known as the nitrate-equivalent mass concentration of a given species (*s*), i.e. the mass of nitrate that would produce an ion current equivalent to that detected for the species (*s*) [*Jimenez et al., 2003b*].

However it has been observed that the direct application of equations 3.6-3.7 underestimates the aerosol sulphate mass concentrations when comparing AMS data to data from other collocated instruments by a factor of 2 [*Drewnick et al., 2003*]. Based on several additional laboratory and field tests [*Allan et al., 2004a*] it is believed that a

significant fraction of the observed underestimation is due to the fact that some ambient particles are irregular in shape and a fraction of them do not reach the vaporiser due to either the known lower focusing efficiency of the aerodynamic lens inlet for non-spherical particles [*Liu et al., 1995b; Jayne et al., 2000; Kane and Johnston, 2000; Tobias and Ziemann, 2000*] or to particle bounce on the vaporiser surface. To characterize these effects, the particle collection efficiency, CE_s, has been defined as the fraction of the sampled particle mass of a given species that reaches the AMS detector [*Alfarra et al., 2004*]. From a physical point of view, CE_s should actually be defined for particles and not species, and in principle could be a function of particle size for particles of the same composition and physical shape. To take into account this effect, equation 3.7 is re-written as:

$$C_s = R_t^{'} C_s^{eq} \tag{3.8}$$

where the only change is the replacement of R_t by R_t' in order to include the particle collection efficiency, CE_s. R_t' is then defined as:

$$R_t^{'} = \frac{1}{RIE_s CE_s} = R_t \frac{1}{CE_s} \tag{3.9}$$

The values of the relative ionisation efficiencies for different species, RIE_s, are obtained from laboratory calibrations of pure species, while the collection efficiencies of different species are inferred from comparisons of AMS data to external measurement techniques.

3.4 AMS optimisation and calibrations

An extensive set of calibrations has to be carried out to ensure that the AMS is operating at optimum performance and producing quantitative results. This section describes all procedures used to optimise and calibrate various parts of the AMS.

3.4.1 Aerosol particle beam alignment

In order to get the maximum possible signal, it is critical to ensure that the particle beam, formed by the aerodynamic lens, is aligned to impact on the centre of the heated

surface (3 mm diameter) in the vaporisation and ionisation cell. This is achieved by calibrating the aerodynamic lens position close to the skimmer between the particle sampling and sizing chambers. The aerodynamic lens is mounted so that the position of its nozzle end is fixed, while the position of the side close to the AMS inlet can be adjusted using a set of two horizontal and two vertical screws attached to a movable plate. This procedure should only be performed once every time the instrument is transported. The procedure requires a constant source of monodisperse particles (typically 350 nm, NH_4NO_3), and a condensation particle counter (CPC). Ammonium nitrate particles are chosen because they can be easily vaporised at the AMS operational vaporiser temperature (500 ^oC), and the 350 nm particle size is selected to ensure that they are transmitted with 100% efficiency (see figure 3.5). The particle generation set up is described in section 4.1. The objective of the procedure is to find the optimum horizontal and vertical positions of the aerodynamic lens by plotting the AMS/CPC % of detected particles as a function of lens position in each case. The positions corresponding to the centres of the resulting top hat curves are selected as the optimum lens position.

3.4.2 Chopper servo position calibration

This calibration is used to determine the open, closed, and chopped positions of the chopper servo. In the open position, the entire aerosol beam accelerating away from the aerodynamic lens is allowed through into the particle-sizing and detection chambers. In the closed position the aerosol beam is fully blocked and the focused aerosol beam impacts on the chopper disc. In the chopped position, only 3.5% of the aerosol particle beam makes it into the instrument every few milliseconds as described in section 3.1.2.

The calibration is an automated routine integrated into the AMS control and logging software, and should only be performed at the start and end of a field study or at the start of a new setup. The procedure includes setting the quadrupole mass spectrometer to scan *m/z* 32 (O_2^+) in the TOF mode of operation, and registering the strength of the signal as the chopper servo position is changed. In this method, the servo positions are selected so that the oxygen signal peaks at the *chopped* position and is at a minimum in both the *opened* and *closed* positions. Measurements are made as the chopper is moved

in both directions (open to closed and closed to open). A large discrepancy in the magnitude of the chopper signal measured in both directions is a sign of chopper servo failure.

3.4.3 Particle velocity calibration

As described in sections 3.1.2 and 3.2.2, the AMS sizes particles by time-resolved particle detection after a known flight distance. Particle velocity can then be calculated and related to its vacuum aerodynamic diameter. In order to relate particle velocity to its vacuum aerodynamic diameter, a calibration curve of known particle sizes and their velocities is needed. It should be noted here that for spherical particles, vacuum aerodynamic diameter is simply defined as the product of the geometric diameter and the particle density, while for non-spherical particles a shape factor needs to be included [*Jayne et al., 2000; Jimenez et al., 2003a*].

This calibration is carried out using monodisperse, commercially available, polystyrene latex spheres (PSL, Duke Scientific Corporation Nanosphere 3000 series, Palo Alto, CA, USA), covering a size range from about 100 to 1000 nm. When using PSLs the vaporiser temperature was set to ~ 750 ^{o}C to ensure rapid vaporisation of the particles. Using a DMA, size selected NH_4NO_3 aerosol particles can also be used after the DMA is calibrated using PSL spheres. During calibration, the AMS is operated in the TOF mode, where the quadrupole mass spectrometer is set to scan one major mass fragment (e.g. *m/z* 104 from PSL spheres or *m/z* 30 from NH_4NO_3). The particle velocity is determined from the ratio of the flight distance, from the chopper assembly to the vaporiser (39.5 cm), to the particle time-of-flight, measured at the peak of the TOF distribution. It has been found that the velocity dependence on the particle vacuum aerodynamic diameter is best described by the empirical expression below [*Jayne et al., 2000*].

$$v = v_l + \frac{v_g - v_l}{1 + \left(\frac{D_{va}}{D^*} \right)^b} \tag{3.10}$$

where ν is the particle velocity (m s^{-1}), ν_l is the axial gas velocity within the aerodynamic lens, ν_g is gas velocity on leaving the nozzle of the lens (m s^{-1}), D_{va} is the particle vacuum aerodynamic diameter (nm), and D* and b are fitted coefficients. Figure 3.10 shows an example velocity calibration curve used to determine the values of the four calibration parameters described above. Once the values of those parameters are known, they are used in equation 3.10 to calculate the vacuum aerodynamic diameters of measured particles.

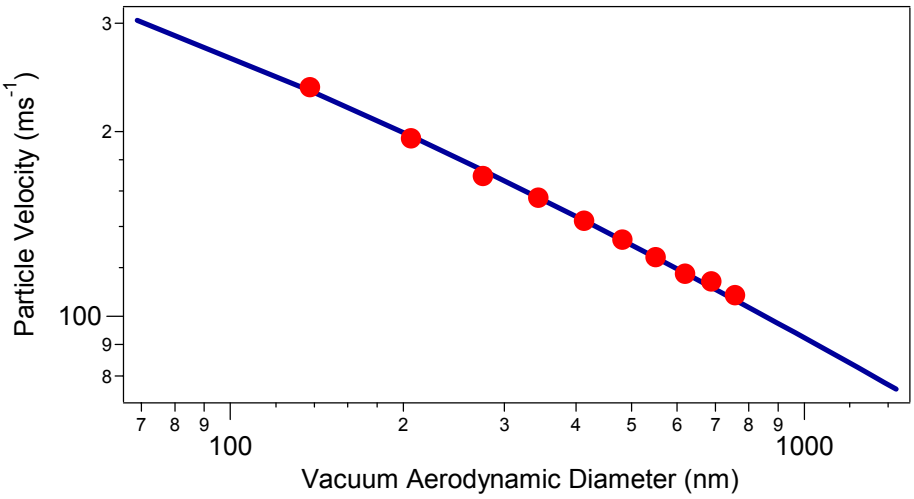

Figure 3.10: Particle velocity plotted as a function of particle vacuum aerodynamic diameter. Data points are from particle TOF measurements using PSL spheres. The solid line is fitted to the data using equation 3.10

3.4.4 Tuning the quadrupole mass spectrometer

This procedure aims to optimise the throughput of ions through the mass spectrometer by tuning the various voltages that control the formation of ions in the ionisation region and their subsequent extraction, and focusing into the quadrupole mass spectrometer, followed by their deflection into the electron multiplier detector. This is regarded as one of the most crucial optimisation procedures that directly affects the ionisation efficiency of instrument and therefore, influences its sensitivity.

A total of eight voltages are applied on various parts in the region between the vaporisation/ionisation cell, at the bottom of the quadrupole mass spectrometer, up to the electron multiplier detector [*Balzers Instruments, 2000*]. The ion reference, cathode and field axis voltages have fixed values and are not, contrary to the rest of the voltages,

part of regular optimisation procedure. The *ion reference* voltage is the nominal potential on which the ions are formed and is the reference voltage to all other potentials. The value of the ion reference voltage is determined once for a new quadrupole and should be kept constant (91 V for the UMIST AMS) as it determines the way the quadrupole operates. The *cathode* determines the acceleration voltage of the electrons and therefore the ionisation energy. The cathode voltage is normally set to 70 eV, which is the standard voltage used in electron impact ionisation mass spectrometry. This allows for AMS mass spectra to be compared with standard available spectra. The *field axis* is the potential in the axis of the quadrupole field. It acts as a decelerating voltage so as to maximise the time the ions spend in the rod system to be resolved. The *extraction* voltage accelerates the ions from the ionisation region towards the quadrupole mass spectrometer system. The *focus* voltage is related to the extraction voltage and one must be optimised when the other changes. Two *deflection* voltages are applied to direct the ions through a 90^{o} turn to reach the electron multiplier detection. An additional voltage, known as the *heater bias*, is applied to the vaporisation and ionisation region to counter the effect of the vaporiser, which is made of a conducting metal, on the field geometries.

The procedure involves maximising the N_2^+ signal by optimising the last five voltages described above. This is automated in the AMS control and data acquisition software and can be set to optimise all five voltages together or one at a time. A successful optimisation routine should result in the maximum ionisation efficiency of standard calibration particles (e.g. NH_4NO_3). The quadrupole tuning should be performed after significant change in the instrument configuration, in particular when the instrument has been exposed to atmosphere. However, the procedure should not be carried out regularly since it will alter the configuration of the instrument and will require a new ionisation efficiency calibration.

3.4.5 Quadrupole resolution calibration (*peak shape*)

The resolving power of a quadrupole mass spectrometer is a measure of its ability to separate two ions of any defined mass difference. Signal can be artificially lost or gained if the resolution is set incorrectly. The resolution of a quadrupole mass

spectrometer determines the peak shape in a way that decreasing the mass resolution results in a poorly resolved, wider peak with higher intensity, while increasing the resolution setting results in a sharper, better resolved peak with lower intensity. The AMS is operated at unit resolution throughout the entire mass scan range and is optimised to ensure that the resolution is set as coarsely as possible to maximise the ion intensity and as finely as necessary to prevent adjacent peaks leaking into each other.

The calibration is based on the following linear function relating the resolution to the individual mass fragments (*m/z*) [*Balzers Instruments, 2000*]:

$$Actual\ Resolution = Resolution\ Setting * (1 + Slope * m/z) \quad (3.11)$$

The quadrupole resolution can be optimised by a two-point calibration at two different mass fragments (*m/z*). It is preferred to use a low mass fragment such as *m/z* 28 (N_2^+) for one calibration point and a high mass like *m/z* 149 (which is typically present as an AMS background peak) to carry out this calibration. The Resolution Setting and slope values are menu parameters that can be varied during calibration until both peaks have the required peak shape and intensity.

3.4.6 Quadrupole mass calibration (*peak position*)

As described in section 3.3, the intensity of a mass fragment in the mass spectrum mode is measured by averaging over a 0.4 amu window set at the flat top of the peak. The quadrupole mass (*m/z*) calibration ensures that those 0.4 amu windows are positioned correctly in order to maximise the measured peak intensity. These positions can be described by a linear equation, 3.12, that relate the scanned mass fragment (*m/z*) to its raw signal as measured on the data acquisition board [*Balzers Instruments, 2000*].

$$m/z = intercept + slope * signal \quad (3.12)$$

Similarly to the quadrupole resolution calibration, the parameters of this linear relationship are determined using a two-point calibration at two different *m/z* values.

This calibration should be checked on a regular basis and corrected if the averaging windows do not correspond to the maximum intensity of peak.

3.4.7 Electron multiplier calibration

The aim of this calibration is to quantify the gain of the electron multiplier and monitor, and compensate for its decrease over time. The gain is a measure of the signal amplification by the electron multiplier. This is an important calibration since the ability of the AMS to produce accurate mass measurements depends on a correct and valid multiplier gain, as discussed in section 3.3.

The electron multiplier gain is optimised by an automated routine, which compares the measured area of the TOF signal from a background single ion with a theoretical area expected for the same ion at the same multiplier voltage. The theoretical area is based on the multiplier gain curve, which relates the multiplier gain to the multiplier voltage as described in equation 3.13.

$$Gain = SF \times 10^{(C_1 + C_2 \times U + C_3 \times U^2)} \tag{3.13}$$

where SF is a scaling factor, U is the multiplier voltage in kV and C_1, C_2, and C_3 are constant coefficients. The coefficients are determined once for a new multiplier by measuring the multiplier signal for single ion events for different multiplier voltages and fitting the results to the curve described by equation 3.13. The values of the coefficients are stored in the acquisition software and used for all subsequent multiplier gain calculations.

The automated gain calibration procedure uses equation 3.13 to calculate the multiplier gain as a function of multiplier voltages. Typically, for low voltages the multiplier gain increases proportionally to the voltage and it levels off for higher voltages resulting in a plateau. In this region of the gain curve, the gain does not increase with higher voltages. The edge of this plateau is the best setting for the multiplier, where the highest gain is obtained at the lowest possible voltage. This produces the best possible signal while extending the lifetime of the electron multiplier detector. The decay in multiplier gain as

a function of time can be accounted for by a scaling factor. The ratio of the measured area of the TOF signal for a background ion to the theoretical value at the same voltage, obtained from equation 3.13, yields the new calibrated scaling factor. Monitoring the strength of the air beam signal either at *m/z* 28 (N_2^+) or *m/z* 32 (O_2^+) provides a good indication of the multiplier performance status. Normally, the strength of those signals is not expected to change significantly as both oxygen and nitrogen have stable ambient concentrations at ground level. As the performance of the electron multiplier deteriorates, the signal strength of these masses decrease and a decision about re-calibrating the multiplier can be made.

3.4.8 Ionisation efficiency calibration (*IE*)

The ionisation efficiency calibration is also known as the mass or nitrate calibration. The purpose of this calibration is to calculate the ionisation efficiency (*IE*) of a material that has a known molecular weight (MW), in order for the (MW/IE) part of equation 3.6 to be accounted for as discussed in section 3.3. Ammonium nitrate (NH_4NO_3) has been chosen as a primary calibration material because of its volatility, which enables near 100% particle vaporisation and does not leave much residue to interfere with subsequent measurements. In addition, ammonium nitrate particles can easily be generated from aqueous solutions and the material is readily available at a reasonable cost.

Ionisation efficiency (*IE*) can be defined as the ratio of the number of ions produced to the total number of available parent molecules for that ion species (e.g. if the ionisation efficiency is $1x\ 10^{-6}$, then 1 molecule in 1 million molecules is ionised). For any given parent molecule, the total number of ions produced can be calculated by a sum of the ion intensities of all its fragment ions. The number of available parent molecules can be determined from the product of the number of moles and Avogadro's number. This can be easily calculated for particles of known size and composition, where density and molecular weight are known.

During a typical AMS calibration, the ionisation efficiency of nitrate (IE_{NO3}) is calculated, using equation 3.14, by determining the number of ions produced per

particle of a 350 nm NH_4NO_3 particles, generated from an aqueous solution and size-selected by a DMA using the setup described in section 4.1 in the next chapter.

$$IE_{NO_3} = \frac{IPP}{\frac{\pi}{6} \times d_m{}^3 \times \rho \times 1e^{-21} \times \chi_v \times f_{NO_3}} \times \frac{MW_{NO_3}}{N_A} \tag{3.14}$$

Where IPP is determined during the calibration by dividing the sum of all nitrate ions by the total number of detected particles, d_m is the mobility diameter of the DMA size selected particles (350 nm), ρ is the density of the NH_4NO_3 particles (1.72 g/cm^3), χ_v is a shape factor (0.8), f_{NO3} is the fraction of NO_3 in NH_4NO_3 (0.775) and N_{AV} is Avogadro's number. The shape factor for NH_4NO_3 particles has been determined empirically [*Jayne et al., 2000*].

The majority of aerosol particles selected by a DMA will be singly charged and have the desired diameter, however a small percentage of particles will be considerably larger than the desired diameter but still be selected (see chapter 2, section 2.3). This happens because the charge distribution on the aerosol entering the DMA approximately follows Boltzmann statistics after passing through the neutraliser. This gives rise to multiple charging phenomenon; where larger particles with 2 charges or more appear to have the same mobility diameter as the singly charged desired particles. However, these particles can be size resolved by the AMS as multiple peaks in the TOF mode of operation, and only particles arriving at the time that corresponds to the singly charged particles are selected for calibration.

The IE_{NO3} calibration is highly influenced by any changes made to the ioniser setup or the quadrupole mass spectrometer. The procedure should be performed following any tuning of the quadrupole mass spectrometer voltages to ensure accurate quantitative results. This calibration should also be carried out at the start of each experiment and needs to be checked every few days of operation.

3.5 Identification of chemical species using the AMS

Off-line analysis methods such as GC-MS employ techniques to separate the chemical components of the sampled aerosol particles before being ionised and detected. This allows for some degree of speciation of the chemical composition of ambient aerosol particles to be obtained. In contrast, the AMS has no such separation methods and it is configured so that the ionisation process is performed on a gaseous molecular cloud resulting from the vaporisation of ensemble of particles. Moreover, the scanning rate of the quadrupole mass spectrometer is not fast enough to scan the full mass range in the time scale of the signal produced by an individual particle. Only one *m/z* is sampled for each individual particle, which means that the signal obtained at a given *m/z* cannot in principle be attributed to a single particle or to specific chemical compound. As a result, three complementary tests are used to identify and verify the presence of specific chemical species (not compounds) in ambient aerosol from the AMS data [*Jimenez et al., 2003b*].

The first test is based on the fact that the AMS utilises a well-established and reproducible ionisation method, for which libraries of mass spectra for thousands of compounds are available. This enables for the AMS fragmentation patterns of inorganic aerosol species, such as NO_3^-, NH_4^+ and SO_4^{--} to be directly measured by sampling particles composed of pure substances and comparing the resulting fragmentation patterns with those observed in ambient aerosol. The second test relies on the time-of-flight data in the form of size distributions at different *m/z* settings of the quadrupole mass spectrometer. Fragments that appear to have similar size distribution shapes, i.e. the signals appear at the same sizes at the same times, together with the fragmentation pattern approach above indicates that these fragments are likely to have the same source. However, these two tests cannot rule out the possible presence of interfering species at a given *m/z*. Therefore, a third test to investigate the presence of interfering species is performed by looking at the correlations in size and mass between fragments corresponding to the same species (e.g. NO_3^- or SO_4^{--}), with deviations from a linear correlation being indicative of significant interference.

Based on the pure species calibration results and after applying the interference detection methodology described above, the sulphate mass concentration is calculated from the MS mode signals of SO^+ (*m/z* 48), SO^+_2 (*m/z* 64), SO^+_3 (*m/z* 80), HSO^+_3 (*m/z* 81), and $H_2SO^+_4$ (*m/z* 98). Nitrate mass concentration is calculated from the MS mode signals of NO^+ (*m/z* 30) and NO_2^+ (*m/z* 46). Ammonium mass concentration is calculated using the TOF mode signal at *m/z* 16 (NH_2^+). Although O^+ and O_2^{++} ions arising from the ionisation of gas-phase O_2 contribute to *m/z* 16, the ammonium and oxygen signals can clearly be separated in TOF mode since gas phase species have much higher velocities than particles. Other fragments of ammonium, such as NH_4^+ (*m/z* 18), NH_3^+ (*m/z* 17) could not be used in the mass calculation due to high background signals from H_2O^+ (*m/z* 18) and OH^+ (*m/z* 17). NH^+ (*m/z* 15) was not included because of low ammonium signal and interference form CH_3^+ arising from organic species. Most of the effort to quantify ammonium and determine interfering ions has been completed by Alice Delia from the University of Colorado, Boulder [*Delia, 2004*]. Organic mass concentration is determined from major peaks detected in the MS mode that are not arising from air molecules, nitrate, sulphate and ammonium. More discussions of the nature of organic species will be presented throughout the rest of this thesis. A description of the method used to compute the mass concentrations of different chemical species, as reported in this thesis, will be described in the next section.

3.6 Data analysis techniques

A suite of analysis tools that can be used for producing quantitative AMS results have been developed at UMIST [*Allan et al., 2003b; Allan et al., 2004b*]. The analysis program has been developed using IGOR PRO; a software package that has its own programming language, supplied by wavemetrics (http://www.wavemetrics.com). The analysis tools have been designed so they can be applied to any AMS dataset, and they are currently in use by most groups within the AMS users community. After loading the AMS raw data from both MS and TOF modes of operation, a number of user-defined corrections can be applied to either or both of them. Figure 3.11 illustrates an example of the "air beam" correction factor, which is applied to account for the degradation of the performance of the electron multiplier detector as a function of time, and therefore a continuous AMS quantitative response can be kept. The principle of this correction is

that the relative degradation should be uniform for all parent chemical species, so a correction factor can be calculated by inspecting the signals of the air beam components (*m/z* 28 or *m/z* 32), which would be constant in ambient air if the multiplier's performance did not deteriorate. This correction factor also takes into account any changes in the sampling flow rate.

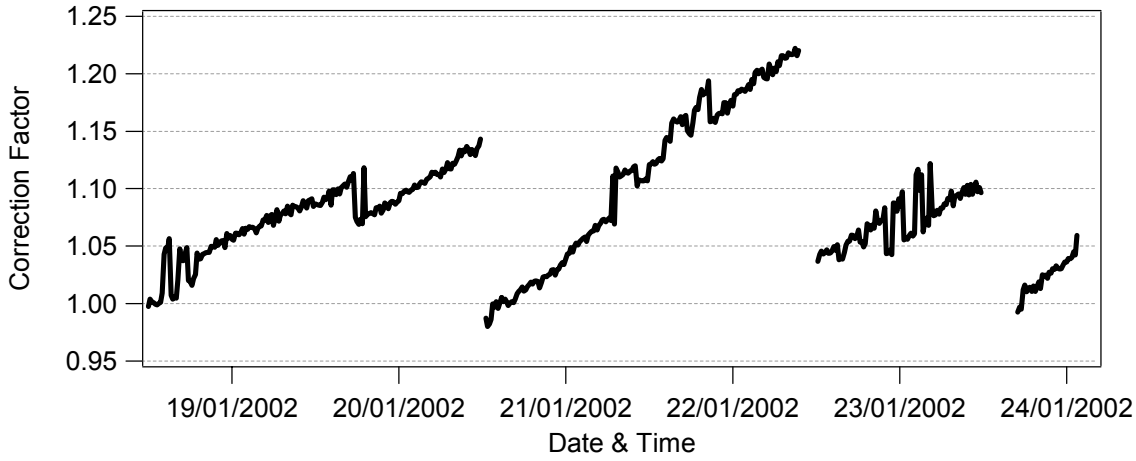

Figure 3.11: An example of airbeam derived correction factor. Note that its value returns to approximately unity after each calibration of the electron multiplier

The program employs the mathematical equations discussed in section 3.3 and the calibrations described in section 3.4 in order to convert detected ions from the mass spectrometer into atmospheric mass concentrations of chemical species in μg m^{-3}. In addition, the program applies the particle velocity calibration data and transforms signals from the TOF mode to chemical mass distributions as a function of vacuum aerodynamic diameters (dM/dlog(D_{va})). Detailed description of the analysis techniques, mathematical calculations and their application to AMS data have been reported elsewhere [*Allan et al., 2003b*].

A generalised method for the extraction of chemically resolved mass spectra from the AMS data has been recently reported [*Allan et al., 2004b*]. The need for such a method has been recognised because interferences between different species in the mass spectrum makes it difficult to identify and quantify aerosol components sampled simultaneously. The method is designed to arithmetically separate the raw data into partial mass spectra of distinct chemical species. This is achieved by employing a user-

definable "fragmentation table" for each chemical species or group of species. These are generated using laboratory derived fragmentation ratios of all species of interest and knowledge of isotopic ratios and instrument performance. When calculating the total mass concentration of a particular chemical species, the total ion rate is calculated by adding up all the peaks as defined in its fragmentation table.

In practice, each table represents a different chemical species, with each row being a mass fragment (*m/z*) in the partial mass spectrum of this species. The user defines the peaks that correspond to each species and their relationships with other peaks in their own partial mass spectrum or in the mass spectra of other species. The content of these tables can vary depending on the specific laboratory or field application, but the underlying methodology remains the same. The fragment tables are shared among AMS users worldwide and are the result of ongoing collaborative research by several groups within the AMS users community. Examples of some of the fragmentation tables used in the analysis of AMS data have been recently published [*Allan et al., 2004b*].