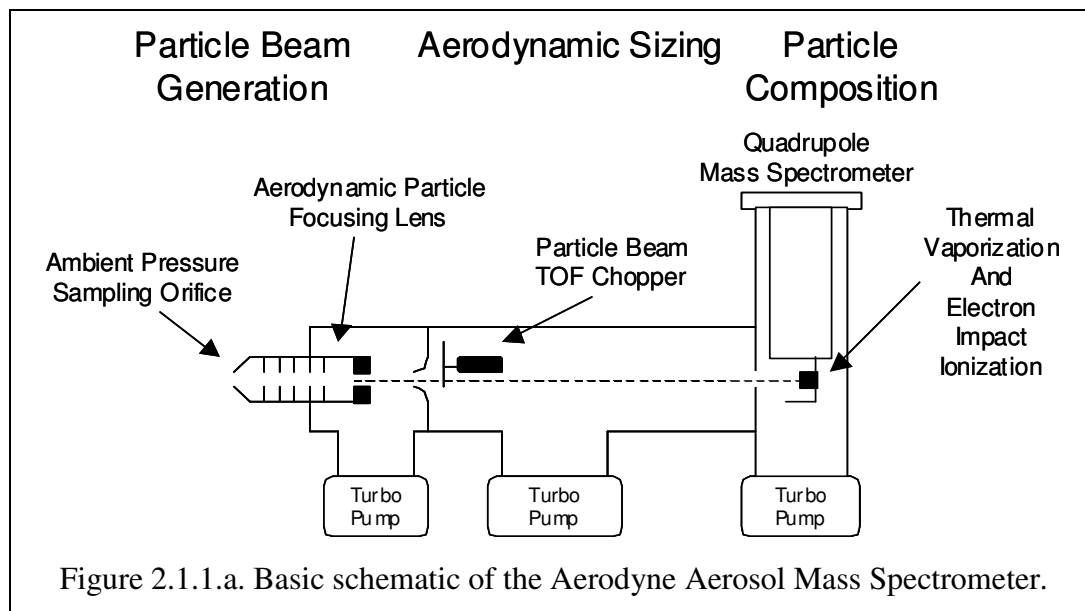


## 2. The instrument and its development

### 2.1. The Aerodyne Aerosol Mass Spectrometer

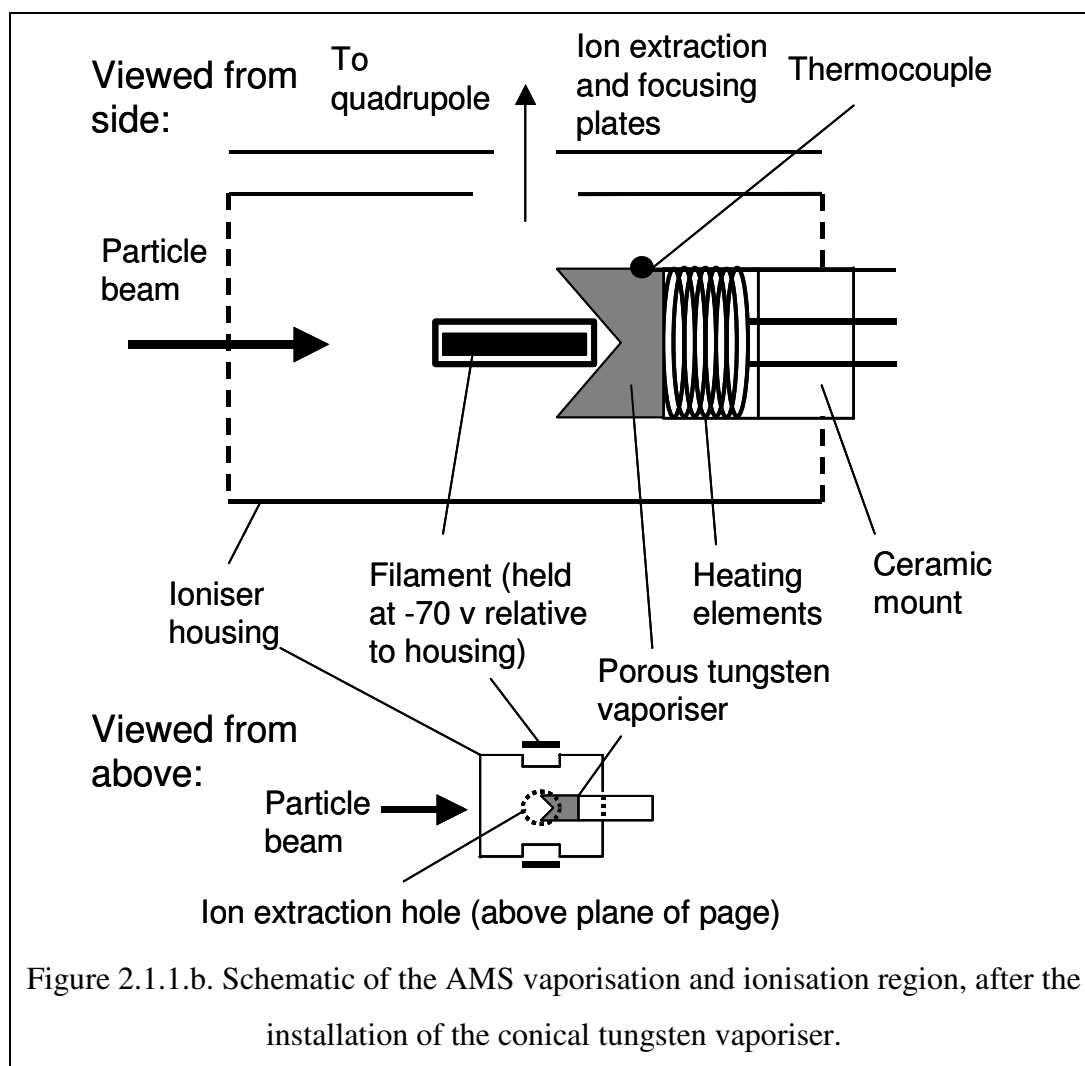
#### 2.1.1. Overview



The aerosol mass spectrometer introduced by *Jayne et al.* [2000] (hereafter referred to as the AMS) and developed by Aerodyne Research Incorporated (ARI), can provide quantitative data on both the non-refractory chemical species present in aerosols and the size of the particles. It is similar in nature to the TDPBMS (see section 1.2.4.2.), in that it uses an aerodynamic lens, thermal vaporisation, electron impact ionisation (EI) and quadrupole mass spectrometry. Detailed descriptions of the AMS and its operation are given by *Jayne et al.* [2000] and *Jimenez et al.* [2003a], but a brief description of the instrument used in the work presented in this thesis is given here.

Figure 2.1.1.a shows the basic layout of the instrument. A critical orifice controls the flow into the instrument, and diameters of 100 and 120  $\mu\text{m}$  have been used, which give nominal inlet flow rates of about 1.5 and 2.0  $\text{cm}^3 \text{s}^{-1}$  at ambient pressure respectively. The flow rate is monitored by a laminar pressure drop element. After the particles have been focused into a beam by an aerodynamic lens (described in section 1.2.4.4.), a skimmer cone removes most of the gas from the sample flow before the aerosol beam enters the second differentially pumped chamber. However, it must be noted that the majority of the mass contained within the beam (by a factor of about  $10^2$ - $10^3$ ) is still gas phase rather than particle phase. The beam then passes a chopper wheel, which consists of a rotating disc with two radial slits positioned on a mount that is actuated by a servo. The chopper can either let the beam pass freely (the ‘open’

position), completely block it (the ‘blocked’ position, used for background measurements) or let small packets of material through at a user-definable rate of 100-150 cycles per second (known as the ‘chopped’ position). The position used depends on the mode of operation of the instrument. The second chamber acts as a time of flight region for particles so their velocity can be calculated from the time taken to reach the detection region after passing the chopper.



The third chamber follows the TOF region and contains a sub-chamber that houses the detection region, where the particles are vaporised on a heated surface, as shown in figure 2.1.1.b. The resulting vapour plume is ionized by EI and then positive ions are introduced into a quadrupole mass spectrometer for filtering according to mass to charge ratio before being detected by an electron multiplier. The signal from the multiplier is fed through a preamplifier to a data acquisition system (National Instruments, Austin, TX, USA) in the logging computer. The voltage is sampled at rates of up to 5 MHz by the data acquisition system and is processed and recorded at a user

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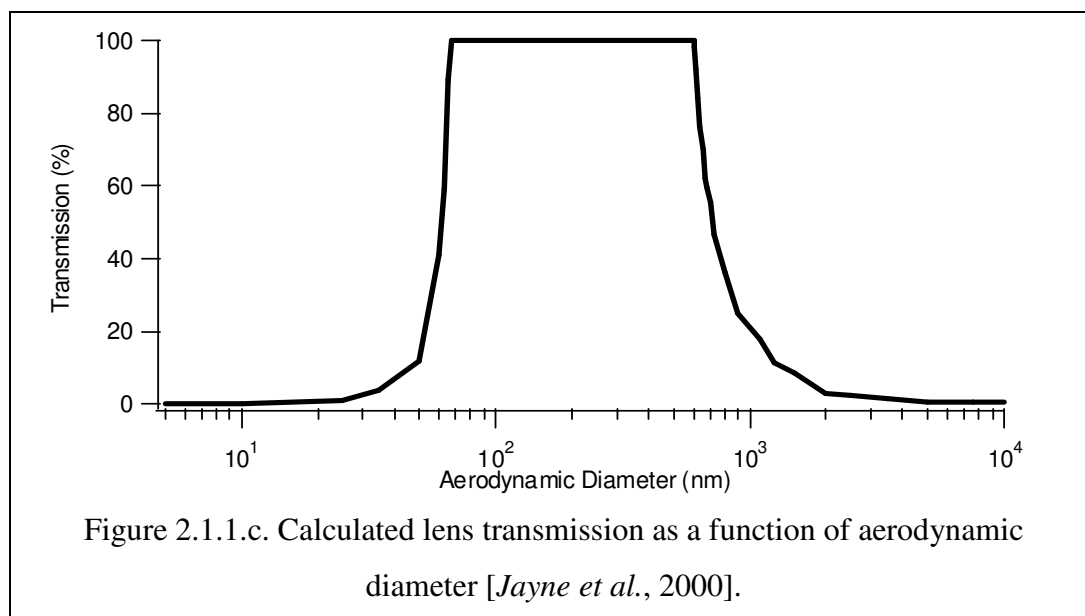
definable rate by the logging software (up to 100 kHz, but 20 kHz was used for the work described here). Detection of ions at the electron multiplier relative to the chopper defines the flight time as long as the vaporisation is rapid and the ionisation process and transmission of the ions through the quadrupole is much faster than the flight time of the particles. For the instrument described with a 0.395 m chamber, the particle flight times range from around 2 to 5 ms, whereas the vaporisation and ion transit times are typically less than 0.1 ms, although larger particles or those composed of less volatile components can take longer to vaporise. The timing resolution is limited by the chopper frequency and the size of its slits. For example, if a 2 % chopper is operated at 120 Hz, this will allow particle flight times to be measured accurate to 0.17 ms.

Each chamber has its own pumping system and the differential pumping of the chambers reduces the sampled gas flow from the lens such that the particle mass is concentrated by a factor of  $10^7$  compared to the ambient air. In this way, with the exception of the major components of air ( $N_2$ ,  $O_2$ , Ar,  $H_2O$  and  $CO_2$ ), there is no detectable interference of vapour components in the measured particulate mass spectrum. In its original configuration, the pumping was performed by five turbo-molecular pumps. Varian Inc. model Turbo-V70LP pumps (Torino, Italy) were used due to their small size, low power consumption and the ability to be operated in any orientation. Two were mounted on each of the first and third chambers and one on the second chamber. The basic principle of a turbopump is fairly simple; it consists of several turbines in series that rotate at such a speed (several thousand rpm), that in order for a gas molecule to reverse flow without striking a vane, it must be travelling at greater than its anticipated kinetic velocity. In order to achieve a sufficient rotational speed, these pumps must be operated at a low pressure (around 2 torr or less), so a backing pump must be used to remove the gas from their exhausts during operation. With the AMS, a diaphragm pump performs this function.

The original inlet system of the AMS used the aerodynamic lens design described by *Jayne et al.* [2000], which is also the same as the lens design used in the TDPBMS [*Tobias et al.*, 2000], as the two instruments were developed in tandem. In its original configuration, the particles between the approximate aerodynamic diameters of 70 and 700 nm are focused with near 100 % efficiency, allowing quantitative study of the majority of accumulation mode aerosol particles (figure 2.1.1.c). A later modification to the lens design reduced the lower cut-off to approximately 30 nm [*Zhang et al.*, 2002; *Zhang et al.*, 2004]. Particles smaller than the lower limit are too

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small to be aerodynamically focused because they tend to behave more like the gas molecules, so the majority are not collimated into the beam. Particles larger than the upper limit tend to impact on the lens stages and the interiors of the tubing through their increased inertia, which results in the transmission efficiency decreasing with increasing diameter beyond that size.



### 2.1.2. Vaporisation, ionisation and analysis

In the detection region, particles are impacted on the vaporiser where they flash vaporise. Initially, a flat molybdenum surface coated with layers of molybdenum mesh was used for this purpose. Temperatures used range from 400 to 950 °C, but are generally kept constant during measurements. 500 to 650 °C is often used as a general-purpose temperature but it can be tailored to specific applications; higher temperatures are better suited to more refractory particles, such as those containing calcium nitrate, but this reduces the overall sensitivity and causes additional molecular fragmentation.

Because the laser pulses used in LDI act to perform both desorption and ionization simultaneously, they must be of a high power, which results in extensive fragmentation of the molecules. Thermal flash vaporization is gentler, so little chemical fragmentation occurs before the constituents are ionised. This also means that low volatility solid particulate matter is not desorbed and therefore not detected, and hence the instrument in the configuration described here cannot measure aerosol components such as crustal material or elemental carbon. Sea salt particles are not generally detected unless the vaporiser temperature is around 850 °C or higher (see section 2.2.1.3.). Particles such as those composed of ammonium, nitrate, sulphate or organic carbon are

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detected efficiently at most temperatures. Those chemicals that can be vaporised within a short enough time scale to be detected correctly within mass spectrum mode (much less than the 5 second alternation time) are operationally described as being ‘non-refractory’, or NR for short.

The EI ionization of the gas-phase molecules is performed using 70 eV electrons emitted from a tungsten filament. Balzers (Now Pfeiffer Vacuum Technology AG, Asslar, Germany) model QMA 400 and later QMA 410 quadrupole mass spectrometers have been used on different occasions to perform the analysis and ETP model 1440 (SGE Inc., Austin, TX, USA) electron multipliers are usually used to detect the ions after filtering. This type of multiplier consists of a chain of surfaces (discrete dynodes), over which a high voltage (normally 1-3 kV) is applied. Incident ions impact onto the first dynode, causing a release of secondary electrons. These electrons progress down the chain to the next dynode, causing the release of more electrons during the subsequent impactations. By the time the cascade has progressed to the end of the chain, the number of electrons released is of the order of  $10^6$ , which is measurable as a current. A preamplifier is used to convert this current to a voltage, which is in turn measured by the computer.

As stated before (see section 1.2.4.1.), a quadrupole mass spectrometer, whilst allowing quantitative data collection [Bley, 1988] and the high time resolution required for particle sizing, does carry the intrinsic limitation that ions of only one  $m/z$  can be studied at any one time. This means that complete mass spectra of individual particles cannot be obtained using this method, but instead quantitative information regarding the entire aerosol ensemble is acquired. Bearing this in mind, the results from this instrument are fundamentally different in nature from those produced by time of flight mass spectrometry instruments and should therefore be viewed as complementary.

### 2.1.3. Modes of operation

In the standard operating configuration, the instrument alternates between two modes, mass spectrum (MS) and time of flight (TOF) mode, by spending typically 15 seconds in each mode during a cycle, although this is user-definable and can be altered depending on the requirements of the experiment. The data are typically averaged over periods of between 2 and 30 minutes. Higher time resolutions have been achieved on mobile platforms by other groups [e.g. Bahreini *et al.*, 2003; Canagaratna *et al.*, 2004], but these sometimes involve additional changes to the standard operating procedure.

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During MS mode, the chopper alternates between the open and blocked positions every five seconds while the mass spectrometer continuously scans, typically from  $m/z$  0 to 300, at a rate of 1000 per second. The logging and control software records the multiplier signal as a function of  $m/z$ , generating mass spectra. A mass spectrum of the particle and gas beam is obtained by subtracting the average mass spectrum acquired when the chopper is in the blocked position from the average when the chopper is in the open position. This removes any contribution from background gas in the detector (the operating pressure in the detection region is  $<10^{-7}$  torr). As this background varies with time, it is important to measure this continuously. In addition to providing qualitative information on the composition of the aerosol ensemble, quantitative ambient mass concentrations (in  $\mu\text{g m}^{-3}$ ) for chemical species can be derived from the mass spectra.

Whilst in TOF mode, the mass spectrometer is set to a single  $m/z$  and sampled at a user-definable rate (20 kHz during the work presented here). The spinning chopper is moved into the chopped position and an optical sensor positioned on the chopper mount senses when a slit is in the position where the aerosol beam is allowed to pass. The multiplier response as a function of time is recorded, starting at this point. The delay time between the particle-laden slug passing through the chopper and the ion detection in the mass spectrometer is the particle time of flight through the system. The time taken between impaction on the heater and detection of the resultant ions is normally of the order of microseconds, which is small compared to the milliseconds taken by the particles to travel the length of the TOF region. By summation of signals in each  $m/z$  channel over many chopper cycles, a measurement of how that reported signal is distributed over particle times of flight can be obtained. As the time of flight is dependent on the particle's vacuum aerodynamic diameter, these data are then used to calculate mass distributions for a particular chemical as a function of aerodynamic diameter.

As well as deriving the mass as a function of particle size, the logging software is also capable of detecting single particles as pulses in the detected signal in TOF mode. Before logging, the software blocks the beam and measures the maximum instantaneous signal level (due to background gases and electronic noise), which it bases a threshold voltage on. During sampling, any pulses above this threshold are counted as single particles. The aerodynamic diameter of the single particle can be derived from its time of flight and the total amount of ions detected from the particle by

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integrating the pulse. The probability that a particle will be successfully detected and counted is based on the mass of the particle and the amount of background at the  $m/z$  being monitored. Generally speaking, only particles with a  $D_v$  greater than around 200 nm are counted reliably, although this varies with the chemical species being studied and its background partial pressure in the detection region.

