
1. Introduction

1.1. Aerosols

1.1.1. The study of atmospheric aerosols

Microscopic aerosol particles are a ubiquitous part of the earth's atmosphere, present in every lungful of air breathed. They are produced in vast numbers by both human activity (anthropogenic) and natural sources and subsequently modified by a multitude of processes. They are known to be crucially important in many issues that directly affect everyday life, which include respiratory health, visibility, clouds, rainfall, atmospheric chemistry and global and regional climate, but they are also one of the more poorly understood aspects of the atmosphere. These shortcomings in our understanding are partly due to their small size, which is typically of the order of microns (10^{-6} m) or less, making them difficult to study, and also the fact that the processes involved are complex. The description of gas phase atmospheric chemistry is by no means straightforward, but the addition of variable, microscopic, condensed-phase components makes understanding the atmosphere and its effects even more challenging, requiring the application of a wide spectrum of scientific disciplines including chemistry, physics, mechanics, biology and medicine.

1.1.1.1. Aerosols and the effect on quality of life

Urban areas have always been known to be a major source of particulate pollution [Colville *et al.*, 2001; Finlayson-Pitts and Pitts, 1997; Mayer, 1999], which is expected to continue to increase due to world population growth and increasing industrialization and energy use, especially in developing countries [Fenger, 1999]. The most obvious effects are the contributions to unsightly smogs [White and Roberts, 1977] and the visible deterioration of building materials [Grossi and Brimblecombe, 2002]. In addition, the fact that urban particulate pollution impacts directly on human health has been known for centuries [Bowler and Brimblecombe, 1992; Brimblecombe, 1987] and has been the subject of much research. Periods of high mortality and morbidity have been linked to elevated levels of particulate pollution [e.g. Dockery *et al.*, 1993; Schwartz, 1994] and research has shown long term exposure to be detrimental to people's health and life expectancy [Nevalainen and Pekkanen, 1998; Pope *et al.*, 2002]. Short term exposure may trigger problems such as heart failure in susceptible

individuals [*Peters et al.*, 2001] and effects such as constriction of the arteries, even in healthy adults [*Brook et al.*, 2002].

In an attempt to reduce the health burden of atmospheric particulate pollution, authorities have attempted to place controls on the total amount of annual pollution and the magnitude of pollution episodes within conurbations. The monitoring of particulate air pollution has traditionally focused on particles of less than 10 μm in aerodynamic diameter (the PM_{10} standard), as these are more likely to pass the throat when inhaled [*Künzli et al.*, 2000; *Larssen et al.*, 1999; *UK Department for Environment Food & Rural Affairs*, 2001] but it has become apparent that the smaller particles are more significant, as these particles will penetrate deeper into the lungs and potentially cause more physiological distress or damage [*Harrison and Yin*, 2000; *Seaton et al.*, 1995]. This has led to the use of the $\text{PM}_{2.5}$ standard in countries such the USA, where the total mass of particulate matter less than 2.5 μm in diameter is monitored [*Environmental Protection Agency*, 1997].

1.1.1.2. The role of aerosols in the global atmosphere

Until recent decades, the chemical properties and processes of the atmosphere has been treated on a purely gas phase basis. Indeed, the majority of matter in the atmosphere is in the gas phase, however the role of particles is proving to be increasingly important in a number of issues. It is insufficient to view atmospheric aerosol particles as merely presenting inert surfaces onto which low volatility products from gas phase reactions condense. Because the components of the particles can be chemically active, the particle population in the atmosphere can present a large surface area on which heterogeneous reactions may occur [*Jacob*, 2000; *Limbeck et al.*, 2003; *Ravishankara*, 1997]. When considering the gaseous fraction of the atmosphere, these processes cause aerosols to become a significant sinks of reactive chemicals and sources of their products. Reactions of this nature include the uptake of nitric acid or its reduction to NO_x , the sourcing or sinking of free radicals such as halogens and the oxidation of VOCs. The abundances of these chemical species are crucially important when trying to predict gas phase processes, for example the production or destruction of ozone. As the individual heterogeneous processes are specific to particles of particular chemical compositions, it is important to have a detailed knowledge of the aerosol climatology before any of these processes can be taken into account in climatology models. Needless to say, it is also important to understand these processes when

considering the behaviour of the particulates, as these reactions can also change their properties with respect to other processes. For example, the nitric acid deposition onto basic crustal particles can radically change their hygroscopic properties.

Particles are frequently aqueous or can act as cloud condensation nuclei (CCN), where they form large, liquid cloud droplets in supersaturated environments, into which gas phase species can dissolve and subsequently react. As aqueous reactions are frequently much faster than the equivalent gas-phase processes, the so-called multiphase processes can act as a significant sink of gases and source of particulate matter. Also, as the reactions take place throughout the particle, they can be limited only to the total amount of the reactants present, as opposed to heterogeneous reactions, which are limited to the surface layer of the particles. An important example of this is the conversion of sulphur dioxide to sulphuric acid in cloud droplets [Calvert *et al.*, 1985; Penkett *et al.*, 1979], which in turn causes problems when deposited such as the erosion of building materials and damage to plant and aquatic life. If a processed cloud droplet dries instead of raining out, the reaction products will remain part of the particle, adding to its mass.

The fact that aerosols are a significant factor in climate forcing has become very well established [Penner *et al.*, 2001; Ramanathan *et al.*, 2001]. Particles in the atmosphere scatter the incoming radiation from the sun, which reduces the radiation flux reaching the surface and has a net cooling effect on the earth [Charlson *et al.*, 1992]. This is known as the direct radiative effect. Also, if there is a larger number of CCN available than there would be otherwise, the larger droplet number concentration in clouds that form will result in them being optically thicker, again scattering radiation to cause a net cooling effect on the earth's surface below (the indirect radiative effect) [Slingo, 1990; Twomey, 1977]. If the cloud particle numbers are elevated, the mean droplet radius will decrease for a given amount of available water. It will therefore be less likely that the cloud droplets will achieve the size needed to become raindrops, meaning that the cloud will have a greater lifetime in the atmosphere. This not only further affects the radiation budgets but also rainfall patterns.

Aerosol particles, particularly those with a high black carbon (BC) content, are also capable of absorbing incoming radiation. While this also decreases the radiation flux at the surface, it heats the atmosphere locally. This heating can in turn cause a third climate forcing effect, known as the semi-direct radiative effect; the heating of the atmosphere can suppress the local relative humidity and thereby reduce the chance of

cloud formation, which would have otherwise caused surface cooling, so the net effect is to increase the amount of energy reaching the surface, the opposite to the direct and indirect effects.

Whether a particle will activate and act as a CCN in a given situation depends on a number of parameters [*Pruppacher and Klett*, 1997, pp. 287-308]. The local conditions such as temperature, humidity and updraught velocity play a big part, as do the physical and chemical properties of the particles. Generally speaking, larger and more hygroscopic particles will more readily form CCN than the smaller and less hygroscopic counterparts. To take the extreme cases, sulphate and sea salt particles make very good CCN whereas those made of unprocessed soot and non-polar organic chemicals will not. The behaviour of particles of mixed compositions, which particles in the atmosphere invariably are after processing, is very difficult to predict, especially when considering the influence of polar organic chemicals [*Charlson et al.*, 2001; *Facchini et al.*, 1999]. This raises the important experimental issue of identifying organic species in particles.

Evaluating and predicting the overall effect aerosols have on the planetary albedo is a challenging problem, not least because of the complexities of the processes involved and gaps in the knowledge surrounding it, but also because there are several theoretical feedback mechanisms intrinsic to these systems. For instance, if an excess of particles causes a net reduction in the amount of incoming radiation reaching the surface in one part of the earth, it would be reasonable to assume that any biogenic processes that act as sources of particles in that region would be suppressed, which in turn would reduce the amount of cooling that takes place elsewhere.

1.1.2. Aerosol properties

Before discussing measurements and instrumentation, it is important to first summarise their mechanics and identify what properties of aerosols are important and of interest. The Encyclopædia Britannica defines an aerosol as “a system of liquid or solid particles uniformly distributed in a finely divided state through a gas, usually air” [2003]. While the particles present in an aerosol experience gravimetric forces that will ultimately cause them to precipitate, these forces tend to be small compared to the instantaneous forces caused by collisions with gas molecules. The random (Brownian) motion that arises from these collisions causes the particles to remain well distributed

through the gas as a colloidal suspension for extended periods of time. Atmospheric aerosol particles are found everywhere and occur in a wide range of sizes.

1.1.2.1. Size definitions

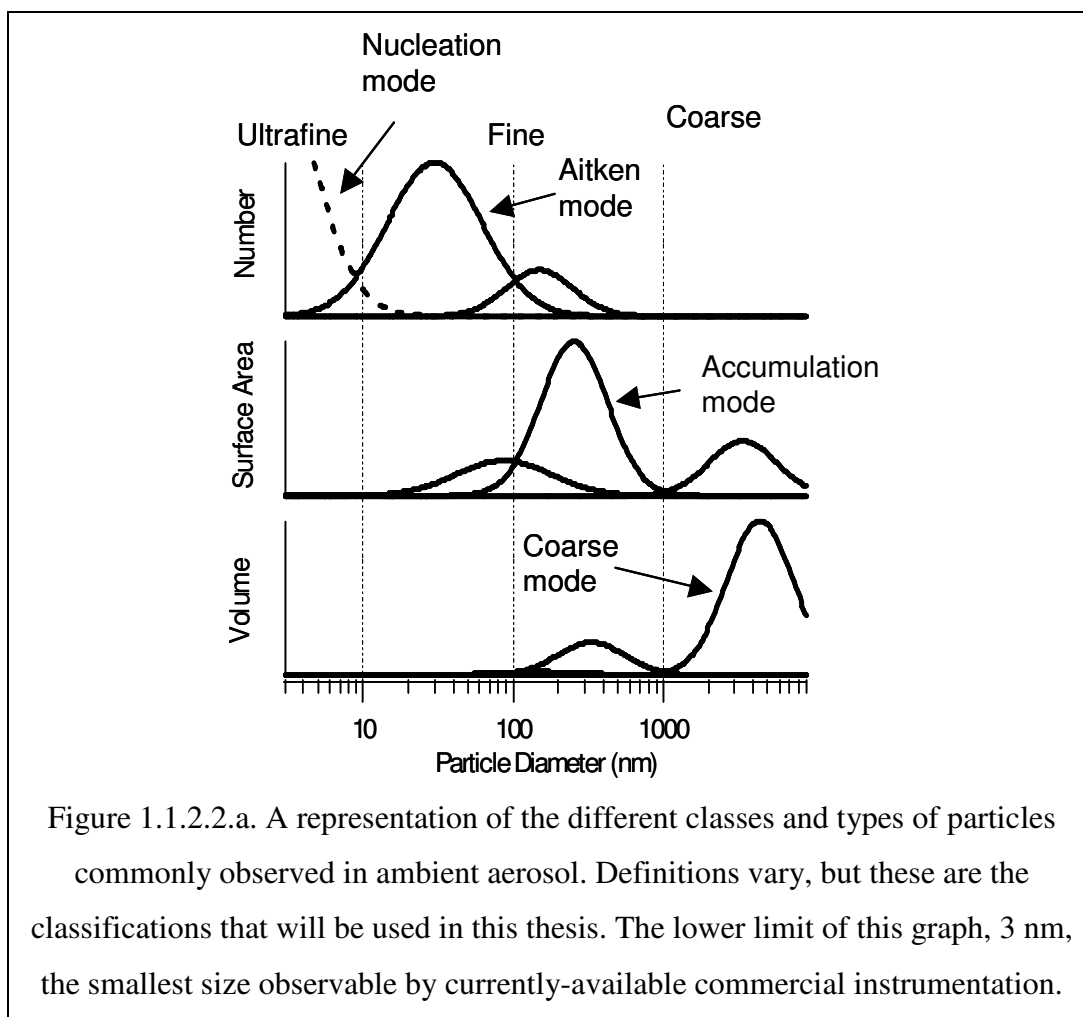
It is important to consider what is meant when defining particle sizes. If all aerosol particles were perfect spheres of uniform densities, it would be simple to define their size as being their geometric diameter. However, this is rarely the case in the real world because particles have widely varying shapes and compositions. The most straightforward measure of a non-spherical particle's size is its volume-equivalent diameter (D_v), i.e. what volume a sphere with the same volume would have. However, there is no universal method of directly measuring this in practice.

An example of a measurable size quantity is the aerodynamic diameter, which dictates how particles behave when moving through the gas they are suspended in. This can be derived from the terminal velocity of a particle i.e. the settling speed at which the particle's gravimetric weight is balanced by the aerodynamic drag it experiences. In addition to the fluid properties of the gas and the acceleration due to gravity, the drag is dependent on the particle's size (D_v) and shape and the weight, dependent on its size and density. The aerodynamic diameter (D_a) of a particle is therefore defined as the diameter of a perfect sphere of unit density (1 g cm^{-3}) that would behave the same way as the subject particle under the same conditions. This property is important not just for settling, as it also governs how particles will behave in systems of rapidly changing flows, e.g. the human respiratory system. The acceleration a particle undergoes when the gas velocity changes is dictated by the drag force exerted on the particle and its inertia, so the same dependencies on size, shape and density are present and the same definition of D_a applies. A related quantity, the Stokes diameter (D_s), is defined as the diameter of a sphere that has the same gravimetric settling velocity as a particle but with the same (as opposed to unit) density.

As will be discussed in section 1.2.1., the various different types of aerosol instrumentation report many different measures of particle diameter, which are each of differing relevance depending on the application of the data produced. Therefore, it is not realistically possible to report a universal measure of particle diameter and in this thesis, the sizing definition will be specified for each diameter reported.

1.1.2.2. Size and source classifications

Atmospheric particles are normally separated into different classes according to their size, as ambient particles normally occupy one of four modes, related to their formation process and atmospheric age (figure 1.1.2.2.a). Exact definitions vary, but the particle classifications that are used in this thesis are as described in this section. The following definitions are normally defined operationally, meaning that the precise physical classification of a given population of particles can vary depending on the instrumentation used to study them.



Much of the total suspended particulate matter in the atmosphere is made up of so-called coarse particles. These are typically classed as those particles of 1 μm or greater in diameter and are normally initially suspended in the air through mechanical processes. These include spray from bubbles bursting in the sea, dust suspended in the air through wind action and debris from vehicular tyre and brake pad wear. Soot particles in smoke and fly ash are a notable exception, because while these can be large enough to contribute to this class, the process creating them is both chemical and mechanical. Biogenic particles such as pollen, spores, airborne bacteria and dead skin

cells also contribute. The particles in this class are frequently the most important when considering the optical properties of the atmosphere, due to their size. They generally have shorter lifetimes in the atmosphere compared to other sizes of particle, as they more are more readily lost through gravimetric settling and impaction (processes collectively known as dry deposition).

The particles of diameters between 0.1 and 1 μm are known as the accumulation mode and tend to be far greater in number concentration than the coarse mode. While some of the particle sources listed above can partly contribute to this fraction, much of the mass comes from gas to particle conversion processes within the atmosphere. Chemicals found in this mode include involatile oxidation products such as sulphate and certain organics and semi-volatile species partitioned with the gas phase such as ammonium, nitrate and some other organics. Accumulation mode particles are generally the most significant when considering gas phase deposition and atmospheric heterogeneous chemistry, as the majority of the chemically active particulate surface area is normally contained within this mode. They also tend to have long atmospheric lifetimes and frequently act as the nuclei for cloud droplets. The ultimate fate of these particles is often loss in rain or other forms of precipitation (wet deposition).

The particles of diameters between 0.01 and 0.1 μm are often referred to as the Aitken mode. These are relatively young particles that can arise from the growth or coagulation of smaller particles and are also produced in high numbers by primary combustion sources such as vehicle exhausts, so are routinely observed as a distinct mode in air that has been affected by these. These particles often continue to grow to accumulation mode sizes through atmospheric processes. Collectively, the accumulation and Aitken mode particles are often referred to as fine particles.

Finally, those particles smaller than 0.01 μm are known as ultrafine particles. These are thought to be formed through nucleation processes directly from gas phase species such as sulphuric acid [Kulmala, 2003; Kulmala *et al.*, 2004]. Because of their small size and mass, these particles are very difficult to study but are normally produced in discrete bursts of very large numbers at their sources. Despite their very low mass, they are extremely significant further downwind when considering particle number concentrations, as these act as the seeds for larger particles. Nucleation bursts can arise in the presence of either biogenic or anthropogenic emissions and favourable local conditions and form a distinct 'nucleation mode' in the particle size distribution. These have been observed in many different environments such as downwind of industrial

stack emissions, forests and coastal tide zones. These particles diffuse rapidly due to their high Brownian velocities and therefore stick easily to any available surfaces through random impactions. If they are not lost through this mechanism, these particles tend to quickly grow through gas to particle conversion or coagulation, so particles of these sizes are never seen as distinct modes far from their sources.

As mentioned before, exact size classifications vary. For instance, within the field of air quality monitoring, the dividing line between ‘coarse’ and ‘fine’ is usually taken to be 2.5 rather than 1 μm . Also, ‘ultrafine’ is sometimes defined as being all particles below 0.1 rather than 0.01 μm . However, the definitions described above are the ones that will be used in this thesis.

1.1.2.3. Other qualities

When considering the composition of aerosols, an important property to note is their mixing state, or how the constituent chemicals are distributed among the particles. For example, if a population of 100 particles is composed equally of two chemical species, species A and species B, it is possible that 50 of the particles are composed purely species A and 50 of species B. This state is known as an external mixture. Conversely, it may also be possible that all 100 of the particles are composed equally of A and B, which is known as an internal mixture. In the real world, there may be many more than two chemicals present and mixing states can be quite complex. However, it is an important property to consider as it greatly affects the aerosol’s physiochemical behaviour. For instance, in an external mixture of particles, the different particle types may be competing for the same gas phase species, e.g. water vapour. This gas phase species may preferentially condense onto one type of particle and not the other.

Another quality is a particle’s structure. If a particle is a well-mixed liquid droplet, it can be considered to be homogeneous but in reality, this isn’t necessarily the case. For instance, solid particles may be created with a degree of structure or undergo subsequent surface processing. Liquid droplets are also not necessarily homogeneous, as they may contain surfactant components that will be concentrated on the surface. It is possible to have mixed-phase particles, such as a solid kernel surrounded by a drop of liquid. These qualities are again very important, as the particle’s surface is where interactions with the gas phase occur. A particle’s shape must be considered too, as this affects its surface area (which in turn affects its chemical properties), its aerodynamic behaviour and its optical properties. Various electron microscopy studies have shown

ambient particles to exist in a wide variety of shapes, such as spherical, crystalline, amorphous, fractal, agglomerate and aggregate.

1.2. Existing instrumentation

Our level of understanding of the nature, sources, processes and effects of atmospheric aerosols has always been limited by the instrumentation that is available to study them both in the field and under controlled laboratory conditions. For a comprehensive review of such instrumentation, the reader is directed to *McMurry* [2000].

1.2.1. Measurement of number, size and mass.

The technology to accurately count, size and determine the mass concentration of particles in real time is well established and many instruments designed to perform these functions have been available commercially for some time. As discussed in section 1.1.1.1., the volumetric mass concentration of particulate matter forms the basis of most environmental monitoring and control worldwide and to perform this measurement, particles can be collected on a filter using suction for offline gravimetric mass measurement.

More recently, beta-attenuation monitors (BAMs, e.g. BAM-1020, Met One Instruments Inc., Grants Pass, OR, USA) have become the standard method of PM_{10} and $PM_{2.5}$ monitoring, as they have a much higher time resolution than is achievable with offline weighing of samples. These collect particles on a filter, where β -radiation is passed through the sample and the reduction in the radiation passing through measured. The degree of attenuation is proportional to the total number of electrons present in the molecules that make up the sample, which to a close approximation is proportional to its total mass. Also used for this measurement is the Tapered Element Oscillating Microbalance (TEOMs, e.g. Series 1400a, Rupprecht & Patashnick Co. Inc., Albany, NY, USA) [*Patashnick and Rupprecht*, 1991], which collect particles onto a filter on the end of a tapered tube, which is vibrated electrically. Changes to the resonant frequency of the system are measured and linked to the mass of the sample. This technique too has very high time and mass resolutions but negates the need for radioactive sources.

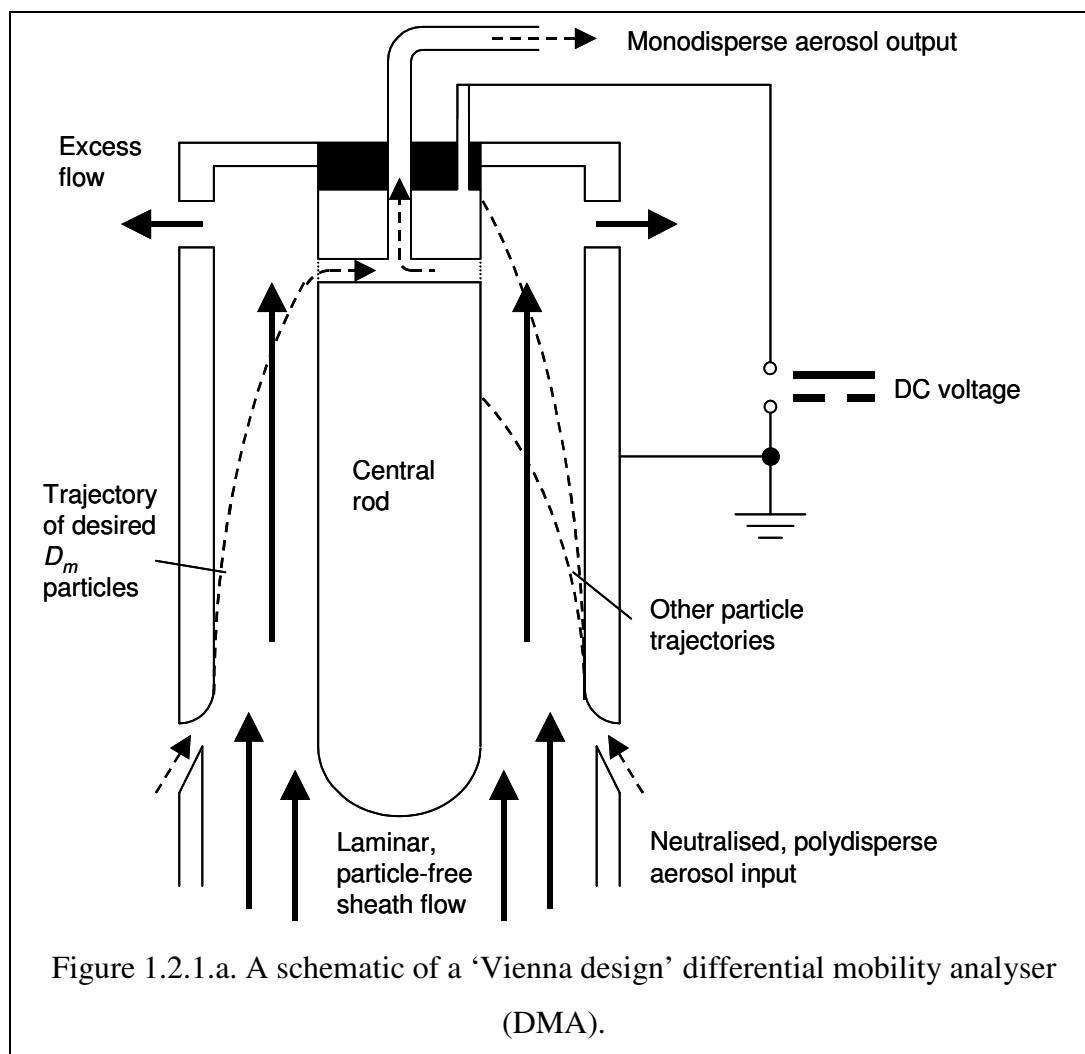
The ability to count particles in real time is also very well established. The condensation particle counter (CPC, e.g. GRIMM Aerosol Technik model 5.403, Airring, Germany), works by growing sampled particles before counting them optically. The earliest versions of these instruments used supersaturated water vapour to

grow the particles but butanol is now the generally the favoured chemical, as it will grow particles composed of both polar and non-polar chemicals. However, recent technical advances have allowed water based CPCs to become more viable (e.g. TSI model 3785, Shoreview, MN, USA), which helps eliminate the use of hazardous chemicals. A diode laser is normally used for the optical counting, with a detector measuring the light scattered from the particles. The size limitation of a CPC is dictated by the fact that particles have to be larger than a certain size before they will activate in the vapour. The smallest detectable particle by a commercial instrument is 3 nm (TSI model 3025a uCPC). It is also possible to derive a limited amount of size and composition data by comparing the pulse heights recorded of the activated particles or by carefully controlling the saturator conditions.

To provide data on particle size as well as number, a common technique involves coupling a differential mobility analyser (DMA, sometimes known as an electrostatic classifier) [Flagan, 1998; Knutson and Whitby, 1975] to a CPC. As an example, figure 1.2.1.a shows the DMA design introduced by *Winklmayr et al.* [1991] (known as the Vienna design), although other versions exist [e.g. Flagan, 2004]. The device consists of a hollow, earthed cylinder with a concentric rod in the centre, to which a positive voltage is applied. Before entering the DMA, the polydisperse (containing more than one size of particle) aerosol sample flow is passed through a neutraliser (e.g. TSI model 3077), which ensures a predictable distribution of charge amongst the particles. A neutraliser normally works by flowing the aerosol past a radioactive source, such as ^{85}Kr or ^{210}Po , which charges the gas molecules present in the aerosol. Particles with positive or negative charges are neutralised by successive collisions with the oppositely charged gas molecules. When equilibrium is reached, most particles are neutrally charged, while a fraction will have a small positive or negative charge of one or more elementary charges (e).

The polydisperse aerosol flow is introduced at the outer edge of the DMA cavity, while particle-free air (known as the sheath gas) is laminarily flowed past the central rod at a volumetric rate of approximately 10 times that of the polydisperse flow. As the combined flow passes up the length of the cylinder, particles with negative charges in the polydisperse flow will migrate through the sheath gas towards the central rod at speeds where the electrostatic force they experience is balanced by their drag forces. The particles that reach the central rod at a particular point are drawn through a

slit, before passing out of the instrument to the CPC. This way, only particles of a given speed are selected for counting.



The speed of a particle in a given electric field, or electromobility, is dependent on its electrostatic charge, its size and its geometry, as well as the properties of the sheath gas it is moving through. A particle's electromobility diameter, or D_m , is defined as the diameter of a sphere with a charge of $-e$ that would have the same electromobility under the same conditions. Note that unlike the aerodynamic diameter, this is completely independent of the particle's density. Also note that for a given D_v , an increase in a particle's irregularity (thereby increasing its drag) will increase its D_m but decrease its D_a and D_s . It is important to remember these differences when comparing data from separate instruments.

DMA's are a useful tool for generating monodisperse (i.e. containing only one size of particle) aerosols and by stepping or scanning the DMA's voltage, a complete size-resolved number distribution can be generated from the CPC data. This is the

principle behind such instruments as the Differential Mobility Particle Sizer (DMPS) [e.g. *Williams*, 1999] and Scanning Mobility Particle Sizer (SMPS) [*Wang and Flagan*, 1990] (e.g. TSI model 3034). These instruments can deliver data with a very high particle size resolution but the time resolution is limited, with complete scans taking of the order of minutes. Artefacts created by the presence of particles with multiple electron charges can be removed at the analysis stage because the positive and negative charges are distributed among the particles in a predictable manner, providing the aerosol reaches equilibrium in the neutraliser. The charging of the larger particles tends to obey Boltzmann's law [*Liu and Pui*, 1974], with equal positive and negative charging, but the distribution of charge amongst those smaller than around 100 nm tends to be uneven, and is better described by Fuchs' theory [*Fuchs*, 1963; *Hussin et al.*, 1983]. Based on these, the numbers of multiply charged particles be predicted based on the measured number of singly charged particles of the same electromobility [*Wiedensohler*, 1988]. DMAs can be tailored to specific applications by altering their geometries and flow rates and can typically analyse particles from nanometres up to the order of a micron in diameter.

To count and size particles of larger diameters, the most common method is to use optical particle counters (OPCs). There are many instruments available commercially (e.g. GRIMM Model 1.104) employing many variations on the technique but the basic principle is to illuminate the particles with a light source, either white (from an incandescent source) or monochromatic (normally from a laser), and measure the light scattered at a particular angle. This technique can provide accurate number concentrations with a very high time resolution and a degree of size information, calculated from the peak scattering intensities. They are normally calibrated by measuring fabricated particles of a known size but the scattering intensities of spheres can be predicted based on Mie theory [*Mie*, 1908] and good agreement has been found between theory and experiment [e.g. *Hinds and Kraske*, 1986]. It must be noted that the size quantity measured by these instruments, the optical diameter (D_o), is dependent on a particle's refractive index (relative to the calibration particles), geometry and internal structure, in addition to its physical size. The lower limit of the detection and sizing is dictated by the intensity and wavelength of the light used and the scattering angle. This technique, depending on the instrument and the technology, can count and size particles from about 100 nm up to several tens of microns. This approach is best suited to measuring spherical particles because irregular particle shapes can generate

unpredictable results, although some instruments can derive extra data on particle shape by simultaneously measuring the scattering intensities at multiple angles [e.g. *Kaye et al.*, 1996].

Another method of counting and sizing simultaneously is the aerodynamic particle sizer (APS, e.g. TSI model 3321). This accelerates particles into a partially evacuated chamber through a nozzle and detects them using two laser beams located at different distances from the nozzle. As well as being able to count and size the particles optically, their velocities can be calculated by measuring the time delay between the detection events of the two lasers, which in turn can be used to calculate their aerodynamic diameters. The advantage of these instruments is that they have a very high size and time resolution, but the particles can become perturbed by the sudden pressure change. In terms of size, they are limited by the fact that the velocities of aerodynamically small particles differ little from the gas phase, so they can typically count and size particles between around 0.5 and 20 μm .

Electron microscopy is a common method of probing particle shape and size; particles are collected before being studied in the laboratory using a commercial instrument such as a transmission electron microscope [e.g. *Dye et al.*, 2000; *Li et al.*, 2003]. However, it does rely on the particles not being significantly affected by the act of collection; they must be immobilised on a film or grid prior to analysis. The particles are also often perturbed by the exposure to the high vacuum that is needed for the analysis, principally by the drying of any aqueous or hydrated component. The recently-developed environmental scanning electron microscope does mitigate this factor, as these are operated at higher pressure (around 10 torr). As the gas present is normally water with a controllable pressure, the partial pressure is comparable to that experienced in the atmosphere.

1.2.2. Analysis of chemical composition

The chemical analysis of aerosols is not as straightforward as the counting and sizing. The most direct method is to pass a sample flow through a filter and analyze the accumulated material in the laboratory using standard analytical procedures. A common method of analysing the collected material is to dissolve the collected material in water and analyse the solution using ion chromatography (IC). This well-established analytical technique quantitatively measures the amounts of aqueous inorganic ions present. However, other aqueous phase analysis techniques are possible, such as proton

nuclear magnetic resonance spectroscopy, which is useful for the identification of functional groups in the water soluble organic fraction [Decesari *et al.*, 2000]. Other techniques include evolved gas analysis, where the material is heated and the resultant gases analysed using any one of a number of gas phase techniques. This is particularly useful for analysing insoluble organic components. The thermo-optical OC/EC analyzer (Sunset Laboratories, Forest Grove, OR, USA) [Birch and Cary, 1996] is a common example of this type of analysis; the sample is first heated in an inert atmosphere (e.g. helium) and the amount of evolved carbon measured to give a measure of the organic carbon (OC), after which it is exposed to oxygen and the subsequent amount of gas phase carbon that is evolved gives a measure of the amount of elemental carbon present (EC). There are also methods that can analyse the sample in place, such as X-ray fluorescence, which is useful for the detection of metals, and Fourier transform infrared spectroscopy, which can be used to identify organic functional groups and structure.

The material used for the filter (the substrate) can be tailored to the intended analytical technique and types in common use include cellulose (paper), PTFE and quartz fibre. While size-selective inlets such as cyclones or impactors can be used to remove unwanted larger particles or substrates with large pores used to allow smaller particles to pass through, it is not generally possible to obtain any detailed size-resolved information using this technique.

A common alternative method of sample collection is the cascade impactor (e.g. MOUDI, MSP Corp., Shoreview, MN, USA). The principle behind an impactor is to direct the sample flow at high speed towards the substrate, mounted on a solid surface. The rapid change in direction as the air passes around the surface causes particles over a certain D_a (dictated by the flow rate, pressure and impactor geometry) to leave the gas streamlines and impact on the substrate. By arranging several impactor stages in series with successively decreasing cutpoints, particles can be separated and collected according to their sizes. Because the substrates do not need to be porous, a wider choice of materials (e.g. aluminium) is available. A problem with the technique is that it relies on the particles sticking to the substrates when they impact; they are frequently known to 'bounce' or otherwise become dislodged after impaction and become re-entrained in the air flow, meaning they may be collected on the wrong stage or not at all. To mitigate this problem, the substrates are sometimes pre-treated or coated before sample collection to promote adhesion. However, these methods are only permitted when the

treatment or coating will not perturb the aspect of particle chemistry of interest or interfere with the analytical procedure being used.

While these bulk sampling methods can employ many powerful and well established analytical techniques to determine the chemical nature of the particles, they carry many intrinsic limitations. Firstly, a measurable amount of particulate material has to be collected and the detection limits of laboratory chemical analysis instrumentation usually require sampling times from several hours to days, so temporal resolution is generally poor. Secondly, because of the intervening time between sample collection and analysis, volatile components of the aerosol may evaporate and be lost or chemically unstable compounds may react in the interim [Chow, 1995; Zhang and McMurry, 1987; Zhang and McMurry, 1992]. Semi-volatile chemicals may also interchange with the gas phase during sampling or before analysis and there is the potential for contamination during handling. Thirdly, while cascade impactors provide some size-resolved information, the resolution is generally poor and particle bounce may result in erroneous size information. Finally, because the aerosol is handled in bulk, no information on the extent of internal or external chemical mixing is retained.

A common remedy for the problem of gas-phase interchanges during sampling is to place a suitable denuder (tubing lined with a reagent) upstream of the collector to absorb any gas phase chemicals that would otherwise contaminate the substrate. A second denuder or chemically treated filter can also be placed downstream and subsequently analysed to measure the amount of particle phase material that has evaporated from the substrate during sampling.

Some of the problems associated with bulk sampling such as gas phase partitioning after collection and contamination during handling can be avoided by performing the analysis in situ by an automated instrument, for example the Series 8400N Ambient Particulate Nitrate Monitor (Rupprecht & Patashnick Co. Inc.). This collects a sample over time through impaction and then through heating, converts the nitrate fraction of a sample to NO_x , which it then measures to calculate a particulate nitrate mass concentration. While this offers an increased time resolution (minutes are possible), it does not deliver size-resolved data and is limited to one aspect of particle chemistry, although instruments employing variations of this principle can be used in parallel used to study other chemical species (e.g. sulphate).

The Particle Into Liquid Sampler (PILS) [Orsini *et al.*, 2003; Weber *et al.*, 2001] is an example of an in situ bulk sampling method that uses a more generalised approach.

Particles are grown to large sizes by introducing them into a supersaturated water environment, and then impacted on a surface, over which water is flowed continuously. The sample water is collected periodically and analysed, frequently using IC, to quantify the amounts of various chemicals present in the aerosol. This allows high time resolution data (minutes) on many ionic components of the aerosol to be collected simultaneously. The disadvantage of this technique, in addition to not providing size-resolved data, is that it is limited to particles that will act as water condensation nuclei. However, the particles that do not fall into this category, for example fresh soot particles, do not tend to contain a significant part of the water-soluble ionic fraction.

1.2.3. Measurement of other properties

The bulk optical properties of ambient particles are of much interest, as these dictate what direct effect they will have on the earth's climate, as discussed in section 1.1.1.2. When a photon interacts with a particle, it may either become scattered, where its direction of travel becomes deflected but is otherwise unaffected, or absorbed, in which case all of its energy is transferred to the particle in the form of heat. To probe the former effect in bulk aerosol samples, integrating nephelometers (e.g. TSI model 3563) illuminate a large volume of sampled aerosol and measure the total amount of light scattered over a wide range of angles. Depending on the instrument design, this measurement can be made for multiple light wavelengths as well. These instruments have been reviewed by *Heintzenberg and Charlson* [1996].

There are many commercial instruments that measure light absorbance by measuring the amount of light attenuated by a sample collected on a filter (e.g. Particle Soot Absorption Probe, Radiance Research, Seattle, WA, USA) [*Hansen et al.*, 1984]. As BC is the most abundant particulate absorber of light in the atmosphere, these probes are often used to provide high time resolution carbon measurements. The agreement between the measured optical absorbances and the predictions based on the carbon measurements provided through other techniques is generally very good [*Turpin et al.*, 1990]. However, while it is the most important, BC is not the only optically absorbent component of ambient aerosols and information on these other chemical species can be obtained using instruments that compare the absorbance at multiple wavelengths (e.g. Magee Scientific Company model AE-31, Berkeley, CA, USA).

These techniques are not without problems, partly because they rely on the assumption that the particles behave the same way on a filter as they do in the air, which

is not always explicitly the case [Bond *et al.*, 1999]. Photoacoustic spectroscopy [Adams, 1988] provides a direct measurement as it takes place in situ while the particles are still suspended. The instrument illuminates the sample with modulated light in an acoustic cell and measures the absorbed energy in the form of sound.

Recent developments in this field also include the Single Particle Soot Photometer (SP2, Droplet Measurement Technologies, Boulder, CO, USA) [Kok *et al.*, 2002], which is capable of in situ black carbon measurements on a particle by particle basis. This illuminates individual particles with a powerful infrared laser and measures not only the scattered light, but also the black body radiation emitted due to the absorbed heat of the particles. By comparing the incandescence at three wavelengths, the temperatures and therefore the BC contents of the individual particles can be derived, in addition to the optical sizes derived from the peak scattering intensities. This has allowed size and mixing state resolved measurements of BC and the high time resolution desired for aircraft deployments.

The hygroscopic behaviour of particles is an important factor because changes in size with variations in humidity alters their optical scattering properties, which in turn affects the direct radiative effect. To probe this specific effect, the humidity of the sample aerosol in nephelometers is routinely monitored and controlled, sometimes using multiple instruments at different humidities during deployments. Hygroscopic behaviour also determines how they interact with clouds [Bower *et al.*, 2000], which in turn affects the indirect radiative effect and the hydrological cycle.

An increasingly common instrument for probing the particle behaviour in subsaturated humidities is the hygroscopicity tandem DMA (HTDMA) [Rader and McMurry, 1986]. In a typical configuration, these size-select ambient particles using a DMA with a dry sheath gas and then flow them through a humidifier. The sample flow is then passed through a second DMA, which has humidified sheath gas (typically at around 80-90 % relative humidity) and selected again according to their size before being counted. By scanning the second DMA, a 'wet' size distribution is obtained for a given 'dry' starting size. Most, but not all, ambient particles will take on water and grow during humidification but the amount that they grow by (the growth factor) is dependent upon their initial size, structure and chemistry. A wet spectrum that contains more than one mode is a good indicator of external mixing within the particles of a given dry size. A second method of data collection is to operate the first DMA at a fixed (high or low) humidity and slowly ramp the humidity of the second DMA up or down

while it is scanned repeatedly. By recording the modal diameters in the different environments, a humidogram is generated, which is the growth factor as a function of humidity for a given starting diameter and humidity. The specific shapes of these curves can again be linked to the particle chemistry and optical behaviour. Some results observed with these instruments are discussed in section 2.1.

Other versions of the tandem DMA configuration exist such as the organic tandem DMA, which grows the particles in an organic chemical (e.g. propanol) instead of water, and the volatility tandem DMA, which subjects the particles to a high temperature between the DMAs rather than growing them. These can be used to obtain further information on other aspects of the particle compositions.

From the perspective of aerosol-cloud interactions, another useful statistic is the number concentration of potential CCN in a given aerosol sample. CCN counters work by subjecting sampled particles to a controlled supersaturated humidity and optically counting the number that are activated [Hudson, 1993]. A common method is to flow the sample past wetted, heated surfaces. As the water vapour diffuses into the sample flow faster than the heat from the surfaces, a region of relative supersaturation is created. The activated droplets are usually detected with a CCD camera. A variation of this concept is the CCN spectrometer, which employs multiple humidities to derive the number of CCN as a function of supersaturation.

1.2.4. Online Aerosol Mass spectrometry

Recently, the field of aerosol mass spectrometry has emerged to provide a real time method for the chemical analysis of aerosol. These techniques overcome the problems associated with bulk collection and offline analysis by analysing the composition in situ on a particle-by-particle basis. The basic principle of an aerosol mass spectrometer is to introduce airborne particles into the instrument, vaporise and ionise the material and then analyse the ions produced using mass spectrometry. For a comprehensive history and review of the majority of instruments that use these principles, the reader is directed to *Suess and Prather* [1999], which covers all the major developments until the end of the 20th century. The reader is also directed to volume 33, issue 1-2 of *Aerosol Science and Technology* (July-August 2000), which is a special issue on the field.

1.2.4.1. Mass spectrometry

The principle of a mass spectrometer is to separate and count ions according to their mass to charge ratios (m/z). Note that for the purposes of this thesis, the m is the mass of the ion relative to the standard atomic mass (defined as one twelfth of the rest mass of a ^{12}C atom, or 1.6606×10^{-27} kg) and z is the charge relative to e , the elementary charge (1.602×10^{-19} C). Therefore, m/z is treated as being dimensionless, although atomic mass units (amu or u), Daltons (Da) and Thompsons (Th) are used as units for the same quantity elsewhere in the literature.

The most basic design of mass spectrometer is the magnetic sector mass spectrometer, which accelerates and focuses ions using electric fields and then bends their paths with transverse magnetic fields. As the ions are accelerated over a specific electrical potential, their velocities, and therefore their deflected trajectories, are dependent on their mass to charge ratios. By using a fixed detector (such as an electrometer), the ions are therefore filtered according to their m/z prior to counting. This type of mass spectrometer can be scanned by varying the electric or magnetic field strengths. While this design is generally not favoured in most current designs of aerosol mass spectrometers due to its bulk, it is capable of very high resolutions, so is often used in other laboratory applications where mass measurements of fractions of amu are needed, such as when identifying specific elements.

Quadrupole mass spectrometers are a more recent design that works by again accelerating the ions using electric fields but this time, the ions are selected by passing them between four parallel rods (figure 1.2.4.1.a). A voltage is applied between the two sets of opposing rods, which consists of AC and DC components. The ions adopt oscillating trajectories as they travel the length of the rods, the magnitude of the oscillations dependent on their mass to charge ratios, the AC and DC voltages applied and the frequency of the AC voltage. Normally, the frequency is kept fixed during operation, as it is easier to vary the magnitudes of the voltages. The AC voltage acts as a high-pass m/z filter, as ions with too low an m/z adopt trajectories with oscillations larger than the spacing of the rods, causing them to strike the rods, become neutralised and not be detected. In a similar manner, the DC voltage acts as a low-pass m/z filter by further perturbing the oscillations of high m/z ions. Therefore, if the two voltages are selected correctly, a quadrupole can act as a filter for all ions but those of the desired m/z [Balzers Instruments, 2000].

Near the end of the rods, the ions are extracted using additional electric fields and detected using devices such as electrometers, electron multipliers or conversion

dynodes. While essentially performing the same function as a magnetic sector mass spectrometer, quadrupoles are much more compact, robust and generally easier to implement, making them ideal for field instrumentation. However, a disadvantage of selecting the ions this way is that the resolving power of quadrupole is limited by the amount of time the ions spend in the rod region, which is typically less than a microsecond. Because of this, the m/z resolution of quadrupole mass spectrometers is typically around unity.

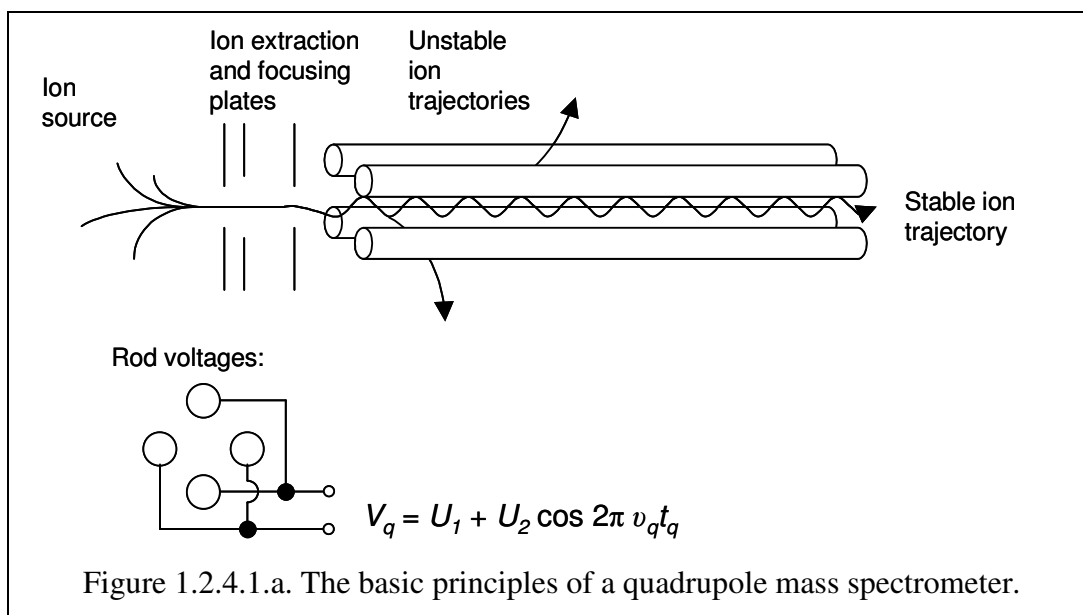


Figure 1.2.4.1.a. The basic principles of a quadrupole mass spectrometer.

A third common type of mass spectrometry is the time of flight method. The basic principle is to again accelerate the ions over a specific electrical potential, but this time measure the time taken to travel a set distance to the detector, from which the velocity and therefore the mass to charge ratio can be calculated. This technique requires accurate timing electronics, rapid data collection and precise gating of the start of the time of flight. However, it does have a major advantage in that ions of many m/z can be detected simultaneously, which is not possible with the previous two methods. This design of mass spectrometer is capable of sub-unity m/z resolution, limited by the spatial and velocity distributions of the ions prior to acceleration, the length of the initial ion pulse and the length of the time of flight region.

Ion traps use a system of two end cap electrodes either side of a ring electrode, which is effectively the rod geometry of a quadrupole wrapped around on itself. By applying the AC and DC voltages between the caps and the ring in the same manner as a quadrupole, ions are indefinitely held in stable three-dimensional orbits between the electrodes. The voltages can be initially set to capture and hold all ions and then

subsequently changed to selectively release ions according to their m/z for detection. Like the time of flight mass spectrometer, this is capable of delivering a complete mass spectrum from a single ionisation event. Also, as the ions remain between the electrodes for longer, it is capable of higher resolutions than quadrupole mass spectrometers. However, because it must be scanned, it takes longer than a time of flight mass spectrometer to deliver a complete mass spectrum.

1.2.4.2. Thermal vaporisation methods

The earliest example of an aerosol mass spectrometer was presented by *Davis* [1973] and worked by impacting particles on a surface heated to up to 1700 °C. The particulate matter evaporated as an ionized elemental gas, which was analysed using a magnetic sector mass spectrometer. This instrument was capable of measuring the amount of a particular element in single particles. Other surface ionisation instruments have been developed over the years, some using quadrupole mass spectrometers instead [e.g. *Davidsson et al.*, 2002; *Jäglid et al.*, 1996; *Myers and Fite*, 1975; *Svane et al.*, 2004].

While it is very sensitive, surface ionisation carries with it inherent problems associated with the fact that different elements ionise at different thermal energies and is also dependent on the work function of the material used for the heated surface, leading to chemical biases. Also, the different components of the particles can interact during ionisation, unevenly distributing the charge. Instruments such as the Chemical Analysis of Aerosols in Real Time (CAART) [*Allen and Gould*, 1981] and the Particle Analysis by quadrupole Mass Spectrometry (PAMS) [*Sinha et al.*, 1982] overcame these problems by separating the vaporisation and ionisation stages; the particulate matter impacts on a surface and is vaporised at a lower temperature as a neutral gas before being ionised using electron impact (EI). Electron impact works by exposing the gas to a cloud of electrons produced from a hot filament and accelerated to a given kinetic energy (normally 70 eV). These electrons randomly strike the neutral molecules and transfer enough energy to cause them to lose one of their own electrons, creating positive ions. Due to the high energies involved, molecular bonds are frequently broken during ionisation, so the resultant ions tend to be fragments of the original molecules. The technique of EI is well established in analytical chemistry and different chemical species create highly reproducible fragment patterns that can be used for identification

[*McLafferty and Turecek*, 1993, p. 6-7]. As the ionisation occurs in the gas phase, the different chemicals are ionised independently of each other.

The Thermal Desorption Particle Beam Mass Spectrometer (TDPBMS) [*Tobias et al.*, 2000] also employs these basic principles. However, it can also be operated in Temperature Programmed Thermal Desorption mode [*Tobias and Ziemann*, 1999], where instead of impacting particles on a heated surface for immediate vaporisation, the surface is initially cryogenically cooled and the particles are collected in bulk. After a large enough sample has been collected, the inlet is closed and the temperature of the surface is slowly ramped while the quadrupole mass spectrometer scans. This means that mass spectral data as a function of chemical volatility is obtained, which can be linked to the vapour pressure, molecular weight and functional groups of the parent species. By carefully comparing the volatility with the signatures seen in the mass spectra, this technique has proved to be very powerful in identifying specific components of organic particles. For example, *Tobias et al.* [2001] were able to report direct evidence that the majority of the organic carbon in particles produced in a diesel engine was due to lubricating oil, as opposed to the products of the incomplete combustion of fuel. Also, *Ziemann* [2002] identified the presence of low volatility diacyl peroxides in particles produced from the ozonolysis of volatile organic species, in addition to the dicarboxylic acids expected.

An alternative method of analysis is chemical ionisation. For example, in Atmospheric Pressure Chemical Ionisation Mass Spectrometry (APCI-MS) [*Hoffmann et al.*, 2002], ions are generated from air using a corona discharge, which subsequently transfer their charge to the chemical species under analysis through processes such as proton transfer. The ionised molecules are then analysed using an ion trap mass spectrometer. This method is primarily designed to study gas-phase organic species, but if these are removed prior to analysis using a denuder and the particles in the aerosol vaporised thermally in the instrument, the particle phase fraction can be studied. As the analysis takes place at atmospheric pressure, there is no perturbation to the particles through exposure to high vacuum. Also, chemical ionisation introduces less fragmentation in the analysed molecules compared to EI, making it particularly useful for the identification and quantification of organic species. However, it is selective, so not all the particulate mass will be accounted for.

1.2.4.3. Laser methods

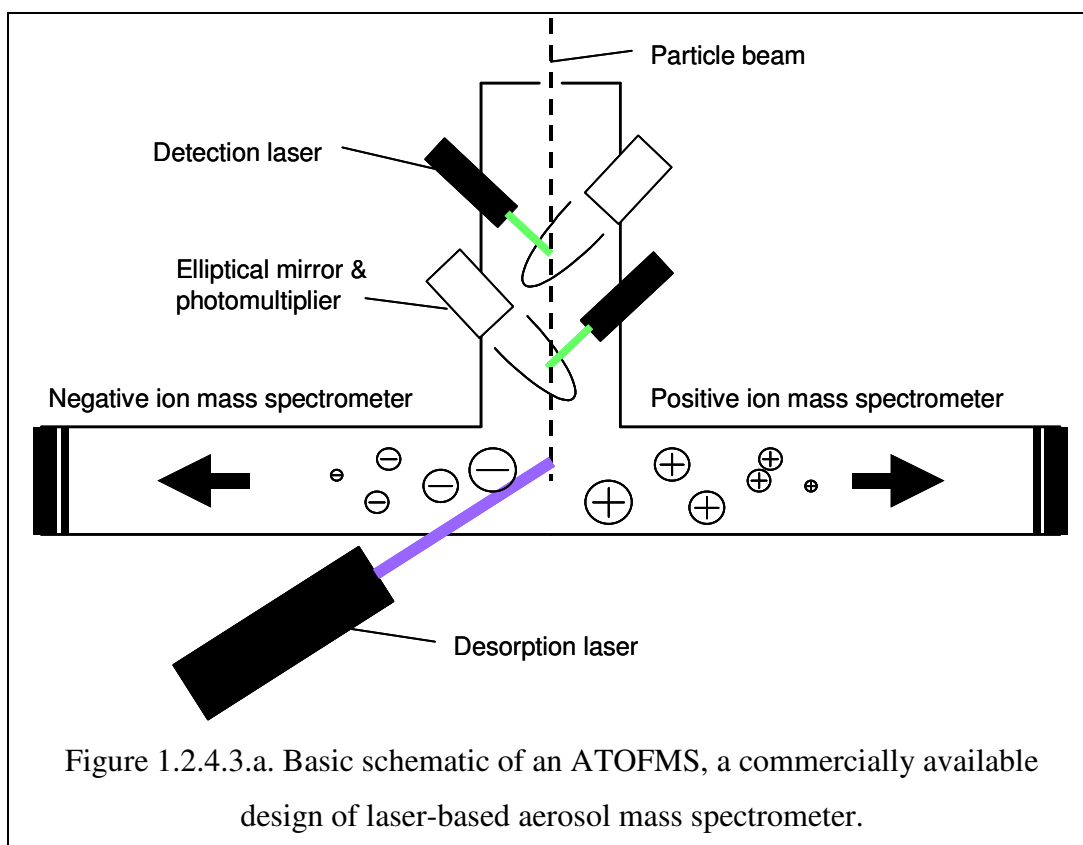
While over the years, the thermal instruments have provided a wealth of new information regarding aerosol particle chemistry, they do have three intrinsic limitations. Firstly, magnetic sector and quadrupole mass spectrometers are only capable of studying one m/z at any one time, meaning that at most, only one particular chemical aspect of any given particle can be studied. While ion trap mass spectrometers can scan multiple m/z , use with EI or chemical ionisation does not possess the time resolution needed to detect individual particles. These factors mean that while these instruments can probe the overall chemical nature of the aerosol as a whole or provide data on single components of individual particles, they cannot directly deliver information on mixing states.

Secondly, the instruments so far described have no direct method of quantifying the size of the particles being studied. This can be inferred by measuring the amount of a particular chemical in an individual particle by integrating the pulses in the mass spectrometer, but while being fairly robust for laboratory-generated particles of known compositions, is of no use for atmospheric particles, where the relative abundances of various chemicals within the particles is unknown. Size-resolved data can be obtained by operating the instruments in series with a DMA, but in order to generate a full distribution, several DMA sizes must be selected consecutively. This means that a complete scan will take an extended period of time and therefore this mode of operation is undesirable for field operation, given that a high time resolution is one of the main aims of aerosol mass spectrometry.

Finally, thermal desorption is limited by the volatility of the chemical components being studied. While chemical species such as ammonium sulphate, ammonium nitrate and organic compounds vaporise readily on the heated surfaces, refractory substances such as elemental carbon and crustal material do not, meaning that these instruments are completely blind to the latter particulate components.

To address these issues, much work over the last decade or so has focused on the use of laser desorption and ionization (LDI), a technique first introduced by *Sinha* [1984]. This technique came into its own when *McKeown et al.* [1991] starting using it in conjunction with a time of flight mass spectrometer. For a summary of the basic principles of this technique, the reader is directed to *Johnston* [2000]. The major advantage of this type of mass spectrometry is the fact that unlike quadrupole and magnetic sector mass spectrometers, ions of all m/z are detected without the need to scan and therefore only a single particle is needed to generate a complete mass

spectrum. Examples of instruments that use this include Rapid Single-particle Mass Spectrometry (RSMS) [Carson *et al.*, 1995; Carson *et al.*, 1997a; Lake *et al.*, 2003], the Particle Blaster [Reents *et al.*, 1995; Reents and Ge, 2000], Particle Analysis by Laser Mass Spectrometry (PALMS) [Murphy and Thomson, 1995; Thomson *et al.*, 2000] and the Aerosol Time Of Flight Mass Spectrometer (ATOFMS) [Gard *et al.*, 1997; Prather *et al.*, 1994], the latter of which is sold commercially by TSI as the model 3800.



The basic principle is to use a high-powered UV laser (typically eximer or frequency quadrupled Nd:YAG) to both vaporize and ionize individual particles simultaneously and obtain a mass spectrum of their components. As the particles tend to be fast moving after introduction into the vacuum of the instrument, a high amount of energy must be transferred in a very short space of time to hit and vaporise them successfully. It has been found that the most effective way of providing enough laser energy has been through the use of Q-switching the desorption laser, which delivers a short, powerful pulse and can also be recorded as the start of the ion times of flight in the mass spectrometer. It is also possible to deliver enough energy to vaporise refractory compounds, permitting the study of particles such as those composed entirely of dust, elemental carbon or meteoric material.

While the laser can be pulsed arbitrarily to randomly hit particles as they enter the instrument, this does not produce a very satisfactory detection rate, so most implementations attempt to detect the presence of the particles through other means first and trigger the high-powered laser pulses accordingly. This requires the use of additional, lower-powered, optical wavelength lasers (such as He:Ne, Ar⁺ or frequency doubled Nd:YAG) to detect the particles as they enter the instrument and travel along the particle beam path. To use the example of the ATOFMS, two detection lasers are focused at different positions along the particle beam, orthogonal to the beam and each other (figure 1.2.4.3.a). Elliptical mirrors and photomultipliers are used to detect the light scattered by the particles. When a particle is detected by both lasers, its velocity is calculated from the difference between detection times and the desorption laser triggered accordingly. The measured velocity of the particles can also be used to determine their sizes, as the amount of acceleration that the particles undergo in the nozzle is dependent on their aerodynamic diameters.

Mass spectrometers can be configured to detect either positive or negative ions, but most are normally operated in positive ion mode, as this tends to yield the information that is most useful for compound identification. However, one advantage of LDI aerosol mass spectrometers is that two mass spectrometers can be used in parallel, configured to extract ions with opposite polarities from the desorption region [Hinz *et al.*, 1996]. This means that instruments such as the ATOFMS can simultaneously capture positive and negative mass spectra for individual particles, increasing the amount of information obtained.

The technique of LDI is not limited to time of flight mass spectrometry. For example, Yang *et al.* [1996] and Reilly *et al.* [1997] presented a laser-based instrument that employs an ion trap mass spectrometer. This also permits tandem mass spectrometry, in which ions of a single m/z are held in the trap and fragmented further using collision induced dissociation. The secondary fragments are then detected using a standard scan. This provides a wealth of additional information about the chemical species responsible for a fragment at a given m/z and is of particular use for identifying organics.

While much qualitative data on the chemical composition of aerosol can be obtained, providing quantitative information with LDI is intrinsically difficult. If the laser fluence (total energy per unit area delivered by the pulse) is high enough for the size of the particle studied, a plasma is formed and all the components are completely

ionised, so the ions can be counted by integrating the pulses observed in the mass spectrometer. Under these circumstances, quantitative data on elementary composition information can be derived [Reents and Ge, 2000; Reents and Schabel, 2001], although any information on molecular structure is lost as the constituents become completely fragmented.

At lower fluences, the molecules remain more intact, allowing more chemical information to be obtained, but at the same time, the particle constituents are not necessarily completely desorbed by the laser pulse and are therefore detected with greatly varying efficiency depending on the particle's size, composition and structure [Allen *et al.*, 2000; Carson *et al.*, 1997b; Kane and Johnston, 2000]. Also, the individual chemical components can interact with each other during the combined desorption and ionisation process, unevenly distributing the charge between the fragments [Neubauer *et al.*, 1998; Reilly *et al.*, 2000]. The causes of this are known as 'matrix effects' and add many extra complexities when analysing data, which are very non-linear and hard to predict.

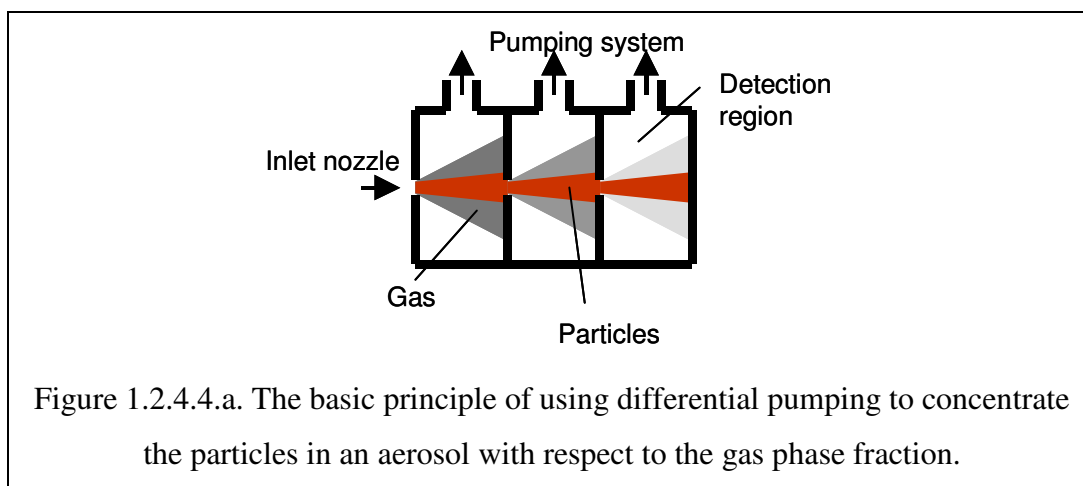
If particles are detected and counted optically, detection is limited by the wavelength of the detection laser, so particles of typically around 200 nm and smaller are not detected reliably. It is possible to study smaller particles by randomly triggering the laser as described above, but this means that the instrument loses its polydisperse sizing capability (although it must be noted that monodisperse sizing is still possible if the particles are pre-selected using a DMA or a specially designed inlet [e.g. Mallina *et al.*, 2000]). Detailed information on organic chemicals is lost due to the extensive molecular fragmentation caused during desorption and ionization, which makes identifying the parent chemicals difficult. Also, aliphatic chemicals and their derivatives are routinely not detected at all, as the presence of a functional group is often required to either absorb the laser photons or obtain a charge [Silva and Prather, 2000]. The two-stage technique introduced by Morrical *et al.* [1998] does mitigate the fragmentation and matrix issues by using two weaker laser pulses to perform the desorption and ionization separately.

Irrespective of these limitations, LDI is proving to be a useful and unique tool for applications such as probing particle structure, performing source apportionment and identifying mixing states and trace elements with a high time resolution [e.g. Ge *et al.*, 1996; Liu *et al.*, 1997; Middlebrook *et al.*, 1998; Murphy *et al.*, 1998; Silva and Prather, 1997]. These instruments tend to produce very large data volumes during ambient

sampling, as individual mass spectra for hundreds of thousands of particles are routinely captured. This has necessitated the development of some innovative techniques for data analysis, normally based around grouping particle mass spectra according to common features and linking these to their compositions and sources [e.g. *Murphy et al.*, 2003; *Phares et al.*, 2001; *Prather et al.*, 2003; *Song et al.*, 1999; *Tan et al.*, 2002].

1.2.4.4. Inlet technologies

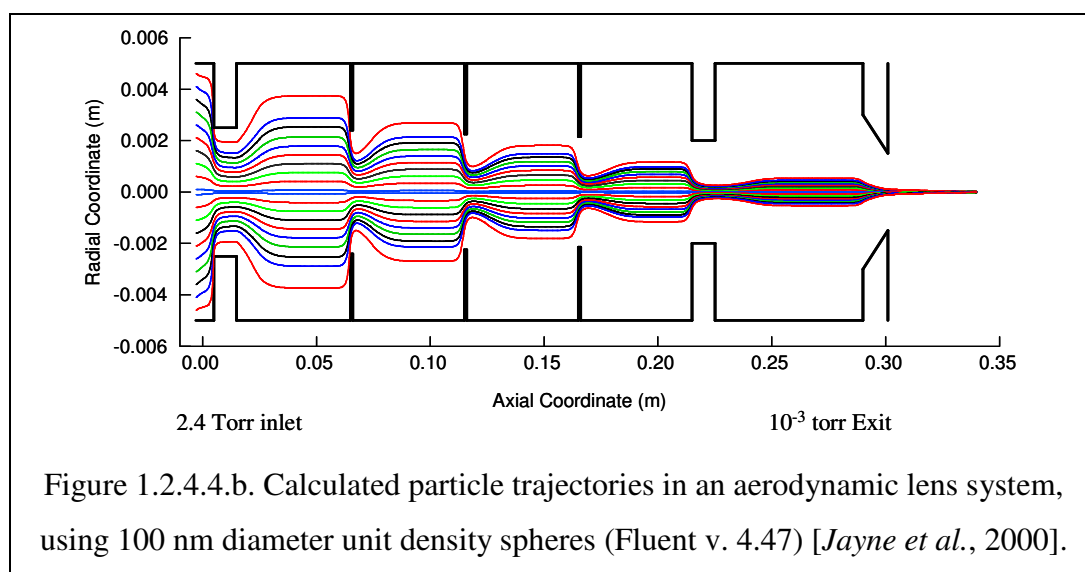
Mass spectrometers must be operated at high or ultra-high vacuum, because random collisions with gas molecules can prevent ions from being detected. Therefore, a key feature of aerosol mass spectrometry involves removing as much of the gas phase material from the aerosol sample as possible while retaining the particulate fraction for analysis. The most common method is to form a collimated particle beam from the aerosol at the inlet and skim off the majority of the gas phase material using a series of apertures and differential pumping (figure 1.2.4.4.a). While the low pressure will perturb the particles slightly, the time between exposure to the vacuum and detection is normally on the order of milliseconds and is therefore too short for this to be a significant problem for most applications, although it is known that some or all of the water fraction of the particle can evaporate during this time [*Buzorius et al.*, 2002]. The previously mentioned APCI-MS is an exception to this, as the vaporisation ionisation occurs at atmospheric pressure.



In most designs, the method of forming the particle beam involves accelerating the particles through a capillary tube or nozzle into the vacuum of the instrument. Due to their inertia, the particulate fraction of the aerosols form a less divergent jet than the gas fraction at the point of expansion. The particles pass through a channel or aperture, allowing the excess gas to be removed by the pumping system.

However, there is still some divergence in the particle beams, with the amount of divergence dependent on the aerodynamic size of the particles. The fact that the particles must hit a physical target or pass through a laser focal point means that there is a tolerance in the solid angle in which particles can travel and be detected. This in turn leads to a measurement bias towards particles of a given size.

In recent years the implementation of aerodynamic lenses prior to a nozzle expansion has sought to address these problems [Liu *et al.*, 1995a; Liu *et al.*, 1995b]. Particles are drawn through a series of concentric apertures with successively decreasing diameters. This causes the gas streamlines to rapidly compress and expand as the aerosol flows through the lens system. These successive compressions cause the particle streamlines to converge on the axis of the lens, so that when they are accelerated through the nozzle, they have small radial components to their velocities and take the form a tightly collimated beam (figure 1.2.4.4.b). As the lens must be operated at a low pressure to reduce defocusing due to Brownian motion, the aerosol must normally pass through a critical orifice before entering the lens.



The main advantage of aerodynamic lenses is that particles over a wide range of sizes are focused into a narrow and very parallel beam, thereby helping to eliminate any size-dependent detection biases an instrument may have over a given size range and improving quantitative capabilities. The tighter beam also increases the number of particles detected, which in turn improves the overall data quality. The previously mentioned TDPBMS uses this technology. Also, TSI have recently started manufacturing an aerodynamic lens (model 3801-030) as an accessory for the ATOFMS. Normally, a particular lens design will have a specific range of particle sizes

it can focus effectively over; smaller particles do not possess enough inertia to be focused properly, so their trajectories tend to follow the gas streamlines. They are also the particles most affected by Brownian motion, which adds an inherently random component to their velocities. Larger particles can overshoot the axis during focusing at a particular lens stage, in effect becoming defocused, or more simply they can impact on the interior surfaces of the lens system during the rapid changes of gas velocity.

1.3. Objectives of this work

The two broad objectives of the work presented here was the development of an Aerodyne Aerosol Mass Spectrometer (AMS) and its application to the study of atmospheric aerosols. This thesis is divided into two sections along these lines (sections 2 and 3 respectively). This is a new aerosol mass spectrometry instrument designed to provide accurate, quantitative and high-resolution data on submicron aerosol particles.

Section 2 covers the instrument and its development. A brief technical description of the instrument is given before the hardware development work that has been performed to further improve its capabilities, sensitivity and accuracy is described. Much of the work presented in this thesis has concentrated on the development of the analysis tools needed to derive meaningful and quantitative data from the instrument. The mathematical principles behind the data processing are presented, along with a detailed description of the calibrations are needed during data collection in order to apply these correctly. The methodology of how these principles have been applied to create a universal data analysis software suite, applicable to different data sets and instruments, is discussed in detail. Finally, work to validate the instrument and its calibration and analysis procedures is presented. This comprises tests performed in the laboratory and systematic comparisons with other instrumentation in the field.

Section 3 covers the application of the AMS to addressing scientific questions regarding atmospheric aerosols through ambient sampling. Due to the amount of operator time and cost involved in operation, the measurements are confined to intensive campaigns at various locations around the world. There are seven campaigns presented, studying ambient aerosols in two types of environments, urban and marine boundary layer. The object of the urban studies is the characterisation and quantification of the aerosols and their production and modification mechanisms within cities. The purpose of the marine studies is again to characterise the particles and their mechanisms within this environment, but also to study how they are transported and transformed over large distances and time scales. An extra section is presented, devoted to the analysis of the organic fraction of the particles, as this is an area of particular interest but about which relatively little is currently understood.

The individual projects themselves can be summarised by the following table (table 1.3.I). The projects will be referred to by name throughout this thesis.

Project name	Section	Date	Location
Urban Studies			
SASUA 3	3.1.1.	November 2000	Edinburgh, UK
Manchester Winter	3.1.2.	January 2002	Manchester, UK
Manchester Summer	3.1.3.	June 2001	Manchester, UK
Pacific 2001	3.1.4.	August 2001	Vancouver, BC, Canada
Marine Studies			
ACE-Asia	3.2.1.	April 2001	Jeju-Do, Republic of Korea
ITCT 2K2	3.2.2.	April 2002	Trinidad Head, CA, USA
NAMBLEX	3.2.3.	August 2002	Mace Head, Co. Galway, Republic of Ireland

Table 1.3.I. Projects referred to in this thesis.