Chapter Two: Aerosol Measurements

2.1 Introduction

Increasing our understanding of the physical and chemical properties of aerosols is vital for properly assessing their effects on various issues such as human health, air quality and global climate and ultimately establishing effective control strategies. However, the identities and concentrations of many atmospheric species, particularly organic components, are still unknown. To characterise the chemical composition of the complex atmosphere, a complementary collection of different analytical methodologies is typically used. Several factors must be taken into consideration when instruments are being developed for these measurements. Ideally, the technique should be fast enough to track changes in concentration, composition, or both as they occur, sensitive enough to detect the species of interest, and free of interferences from other species present in the same air mass. Further consideration may include the weight and portability of the developed instrumentation. The physical and chemical measurements of atmospheric aerosols have been recently reviewed in a number of publications [*Chow, 1995; Spurny, 1999; McMurry, 2000*]. This chapter discusses established as well as recent instruments in the field of atmospheric aerosol measurements with a particular focus on measurements of aerosol chemical composition as well as aerosol mass spectrometry.

2.2 Measurements of aerosol mass and number concentrations

Measurements of aerosol mass concentrations are important for regulatory and scientific reasons. Most of the national ambient air quality standards for aerosols are based on the mass concentrations for particles smaller than 10 μm in aerodynamic diameter (PM_{10}). More recently, countries like the United States introduced similar standards for particles smaller than 2.5 μm in aerodynamic diameter [*EPA, 1997*]. Therefore, particle mass concentrations are routinely measured in monitoring stations in various locations around the world. A commonly used technique for measuring particulate mass concentrations involves filtration [*Chow, 1995; Spurny, 1999; McMurry, 2000*]. Filters are weighed under controlled temperature and relative humidity conditions before and after sampling, and mass concentrations are determined from the increase in filter mass and the volume of air sampled. Filter samplers are most commonly equipped with inlets that

eliminate particles above a specified size cut. Factors including adsorption/desorption of water and reactive species by the filter media and particle losses associated with handling lead to high uncertainties in this type of gravimetric measurement.

Automated instruments for measurement of aerosol mass concentrations have been commercially available for some time and a number of them have been designated by the EPA as equivalent methods for measuring PM_{10} and $PM_{2.5}$ mass concentration. Beta gauges (e.g. BAM-1020, Met One Instruments Inc.. Grants Pass, OR, USA) are increasingly used for PM_{10} and $PM_{2.5}$ mass concentration monitoring due to their advantageous high time resolution and automation compared with gravimetric mass measurements. They measure the attenuation of β-radiation through a particle-laden filter, which results from scattering of the β-radiation by atomic electrons in the filter media and by the deposited particles. The degree of attenuation is proportional to the total number of atomic electrons in the sample, which to a close approximation is proportional to the total sample mass. Another instrument utilised for this measurement is the Tapered Element Oscillating Microbalance (TEOM, e.g. Series 1400a, Rupprecht & Patashnick Co. Inc., Albany, NY, USA) [*Patashnick and Rupprecht, 1991*]. The unique component of the TEOM is a tapered tube, the wide end of which is mounted on a rigid base. Particles are collected on a replaceable filter that is mounted on the narrow end of the tapered tube, which is free to oscillate. The tube vibrates at a frequency that depends on its geometrical and mechanical properties and on the mass of the filter. Changes in the tube's frequency of oscillation are measured and related to the mass of the sample. TEOMs not only provide automated, highly time-resolved mass measurements (like beta gauges), but also operate without radioactive sources.

Instruments, which count aerosol particles in real-time and at high time resolution are well established. The condensation particle counter (CPC, e.g. TSI model 3010, TSI Inc., Shoreview, MN, USA) measures the total aerosol number concentration larger than some minimum detectable size. They work by growing particles by condensation in a supersaturated environment until they are sufficiently large to be detected optically. A variety of substances have been used as the condensing vapour, but *n-* butyl alcohol and water are the most common. CPCs can detect individual particles as small as 3 nm (TSI

model 3025A, TSI Inc., Shoreview, MN, USA), so they provide an extraordinarily sensitive means for detecting small amounts of material. Because the supersaturation of the condensing vapour is very high, the response of CPCs is typically insensitive to the composition of the measured particles.

2.3 Aerosol size-resolved measurements

The size of aerosol particles is of crucial importance to their impacts on human health and global climate (see section 1.1.2). Particle sizing measurements have been carried out using a number of methods using a variety of approaches. As a result different sizes can be reported for the same particle depending on the technique utilised. Differential mobility analysers (DMAs, also known as electrostatic classifiers) [*Knutson and Whitby, 1975; Winklmayr et al., 1991; Flagan, 1998*] classify particles according to their electrical mobility, which depends on gas properties, particle charge, and the geometric particle size but is independent of the other particle properties such as density.

The DMA (Figure 2.1) consists of a hollow, earthed cylinder with a concentric rod in the centre, to which a positive voltage is applied. The input polydisperse aerosol (containing more than one size of particles) is first passed through a neutraliser (e.g. TSI model 3077) to ensure a predictable distribution of charge amongst the particles, where most particles are neutrally charged, while a fraction will have a small positive or negative charge of one or more elementary charges. Particles are then introduced into the electrostatic classification section, where a laminar flow of particle-free air (known as the sheath gas) flows past the central rod at a volumetric rate of approximately 10 times that of the polydisperse flow. As the combined flow is travelling axially between the central rod and the cylinder, particles with negative charges in the polydisperse flow migrate through the sheath gas towards the central rod at speeds where the electrostatic force they experience is balanced by their drag forces. At a particular point along the central rod is a gap that allows a small airflow to leave the classifier and exit through a central tube. Only particles with a narrow range of mobilities can enter the gap. Particles with greater mobilities migrate to the central rod before reaching the gap, while those

with lower mobility go beyond the gap and are extracted out. Adjusting the voltage on the central rod and the flows inside the DMA controls the size of the exiting aerosol.
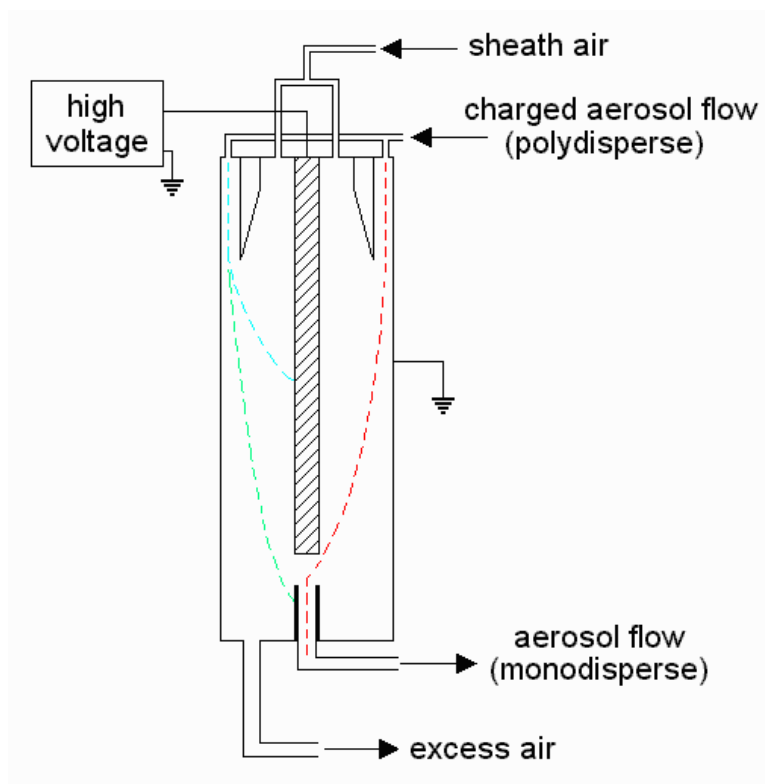

Figure 2.1: A basic schematic of a differential mobility analyser (DMA)

Using a CPC for particle detection, and the act of stepping or scanning the DMA's voltage can generate a complete size-resolved number distribution. This is the principle applied in instruments such as the Differential Mobility Particle Sizer (DMPS) [*Williams, 1999; Williams et al., 2000*] and Scanning Mobility Particle Sizer (SMPS) (e.g. TSI model 3034). These instruments are widely used to measure size distributions in the 3 – 1000 nm diameter range at a very high size resolution. However, the time resolution is limited to the period required to carry out a complete scan of the range of sizes required which can take up to several minutes. Artefacts caused by the presence of particles with multiple electron charges can be corrected for at the analysis stage because the positive and negative charges are distributed amongst the particles in a predictable manner, providing the aerosol reaches equilibrium in the neutraliser [*Liu and Pui, 1974*].

Optical particle counters (OPCs) are the most common method for counting and sizing large particles of up to several tens of microns in diameters (e.g. GRIMM Aerosol Technik model 1.104, Ainring, Germany). The basic principle of OPCs is to measure the amount of light scattered by individual particles as they traverse a tightly focused beam of light. A fraction of the scattered light is collected and directed to a photodetector, where it is converted to a voltage pulse. Particle size is determined from the magnitude of this voltage pulse by using a calibration curve usually obtained from measurements using spherical particles of known sizes and refractive index. Typically particles less than 0.2 μm in diameter are not big enough to produce signals above the noise level. Light-scattering techniques have the advantage of minimally disturbing the aerosol and providing instantaneous information that is often suitable for continuous monitoring. A disadvantage of light-scattering instruments when they are used for atmospheric measurements is that the particle properties (shape, refractive index, and morphology) required to determine size from pulse data are typically unknown. Even for the ideal case of homogeneous spheres, uncertainties in the knowledge of particle chemical composition can lead to significant uncertainties in estimates of refractive index.

The aerodynamic particle sizers (APSs, e.g. TSI model 3321) are another method of simultaneously counting and sizing particles. As an aerosol is rapidly accelerated through a nozzle into a partially evacuated chamber, particles tend to lag behind the carrier gas due to inertia [*Wilson and Liu, 1980*]. The difference between the particle and gas speeds increases with size and density since inertia increases with these properties. Aerodynamic particle size is inferred from particle velocity, which is determined by measuring the time of flight taken by the particle to travel a known distance. Unlike optical counters, which determine particle size from the intensity of the scattered light, aerodynamic particle sizers simply use the scattered light to detect particles at both ends of the flight distance. The smallest reported size that can be measured with these instruments varies with instrument design and ranges from 0.2 – 0.5 μm in diameter. These instruments are capable of providing high-resolution information on aerodynamic size distribution in real time. However, the cooling and pressure drop associated with expansion of the flow into vacuum can lead to a change in

relative humidity and may therefore affect measurements of particle size and possibly particle number if the particles are entirely composed of semivolatile material. Sizing errors also occur due to deformations in the shapes of liquid droplets. Insufficient attention has been given to these phenomena to permit an estimate of measurement error, but errors are likely to be significant, especially at high humidities [*McMurry, 2000*].

2.4 Measurements of aerosol chemical composition

Determining the chemical composition of ambient aerosols is much more complicated than counting and sizing them. This is largely because atmospheric aerosols (in particular the organic fraction) can contain up to hundreds of compounds spanning a wide range of chemical and thermodynamic properties [*Saxena and Hildemann, 1996*]. Conventionally, aerosol chemical composition measurements involve the off-site laboratory chemical analysis of deposited particles some time after sample collection. However, movement towards on-line sample collection and analysis has, recently, taken place.

2.4.1 Off-line methods

Measurements of particle composition using off-line methods typically involve the collection of particles on substrates for a defined period of time using different sampling techniques such as filters, impactors and denuders (see below). The collected samples are then transferred to a laboratory for extraction and chemical analysis. Sampling times vary with ambient loadings, sampling rates and analytical sensitivities but typically vary from several hours in urban areas to a day or more under clean background conditions. Several off-line analytical techniques are available for analysing the composition of collected particles such as atomic absorption, scanning electron microscopy (SEM), high performance liquid chromatography (HPLC), gas chromatography (GC), ion chromatography (IC), proton nuclear magnetic resonance (HNMR), secondary ion mass spectrometry (SIMS), inductively coupled plasma mass spectrometry (ICPMS), and laser microprobe mass spectrometry. For more details on the application of these methods to aerosol chemical composition analysis, the reader is directed to the following references [*Chow, 1995; Spurny, 1999; McMurry, 2000*].

The most common approach for determining the composition of atmospheric aerosols involves the analysis of sample deposit collected on filter substrates. While filter samplers are inexpensive and relatively simple to use, they require manual operation and the number of filters that must be analysed in a monitoring network or in an intensive field campaign can be large. Furthermore, they can only provide size information by using filters with different pore sizes in series and this only delivers very coarse resolution. *Chow* [*1995*] provides a comprehensive treatment of the use of filters to determine the chemical content of particulate matter, where suitable filter materials for various analytical methods and species sampling artefacts are discussed.

Impactors use a variety of film and foil substrates to collect particles classified according to their aerodynamic diameters on a series of stages, each with a successively smaller cut size. The chemical composition of the size-resolved aerosol samples can then be determined using a variety of analytical techniques. Classifying particles according to aerodynamic diameter is ideal for health effects studies since lung deposition of particles larger than a few tenths of a micron depends on aerodynamic diameter. Impactors that collect particles down to 0.05 μm are now used routinely, examples of which include the Berner impactor [*Berner et al., 1979*] and the MOUDI cascade impactor (the Micro Orifice Uniform Deposit Impactor, Applied Physics Co., Niwot, CO, USA). Particle bounce is an inherent problem with impactors. Coated substrates largely eliminate bounce and are commonly used for atmospheric sampling [*McMurry, 2000 and references therein*]. While coatings that do not interfere with some types of chemical analysis have been found, no available coating is compatible with measurements of the particulate organic carbon content.

A variety of impaction substrates have been used for ambient aerosol collection with impactors [*Chow, 1995*]. Aluminium foil is often used for samples that are going to be analysed for organic and elemental carbon (OC/EC), because these substrates can be pre-cleaned to reduce the carbon blank to very low levels. Pre-cleaned Teflon or Mylar film is used when ion chromatography is the analysis technique, as ion blanks can be made very low on these surfaces. Teflon membrane filters have also been used as impaction surfaces. Although these are more expensive than film or foil substrates, they

do not require pre-cleaning, and are more suitable for non-destructive analytical methods such as x-ray techniques.

When using filters or impactors, a variety of sampling artefacts can affect the measured composition of the collected particle deposit relative to what was actually in the atmosphere. Volatilisation of semivolatile compounds (compounds that are found in both the vapour and particulate phase) is known to be a significant source of negative error for species like ammonium nitrate and many organics [*Katz and Chan, 1980; Wang and John, 1988*]. Volatilisation can occur because of pressure reductions in the sampler, which upset the equilibrium between the deposited particles and the vapour, or due to changes in temperature, relative humidity or composition of the incoming aerosol during sampling. Adsorption of gas-phase compounds (e.g. organics) onto filters during and/or after sample collection is a source of positive error [*Turpin et al., 1994*]. Particles bouncing off the collection substrate of an impactor stage during sampling lead to incorrect size classification [*Stein et al., 1994*]. Artefacts associated with sampling transport and storage have also been reported [*Chow, 1995*]. Estimates of artefact contributions to organic carbon (OC) mass measurements range from −80% for volatilisation-induced bias to +50% for adsorption-induced bias [*Turpin et al., 1994*]. Evaporative losses of particulate nitrates have been investigated in the laboratory by a parallel sampling of ammonium nitrate particles with a Berner impactor and a Teflon filter [*Wang and John, 1988*]. The sampled air emerging from both samplers was subsequently passed through nylon filters to collect evaporated nitric acid. Losses from the impactor were $3 - 7\%$ at 35 ^{o}C and 18% relative humidity, and losses from the filter were $81 - 95\%$ under the same conditions.

In order to overcome some of the artefacts associated with measuring semivolatile compounds, diffusion denuder-based sampling methodology has been introduced [*Possanzini et al., 1983; Eatough et al., 1995; Lane and Gundel, 1996*]. With this approach, the vapour phase diffuses and sticks to an adsorbent surface (e.g. activated carbon, special polymer resins) upstream of the particle filter (the upstream surface being known as the denuder). The removal of the gas phase disturbs the gas-particle equilibrium, driving volatilisation of particulate material from the filter. Therefore,

another adsorbent bed (filter or cartridge) for collecting gases must be included downstream of the filter. In this system the gas phase is collected in the denuder, and the particle phase is the sum of the material collected on the filter and the adsorbent surface downstream, assuming that the adsorbent collects all of the volatile and semi-volatile material that evaporate off the particle sample on the filter. Diffusion denuders have been successfully used to distinguish inorganic gas phase species such as nitric acid and ammonia from their particulate forms [*Shaw et al., 1982; Koutrakis et al., 1993*]. Application of the diffusion denuder technology to semivolatile organic compounds is an active area of research and shows promise for this difficult measurement. Because there are a wide variety of semivolatile organic compounds with varying adsorptive properties, finding the ideal denuder coatings is a nontrivial task. As a result, denuder systems are most frequently used for the measurement of specific classes of organic compounds (e.g. PAHs and pesticides) by selecting the right adsorbent material.

Although the use of denuder-based samplers overcomes some of the sampling limitations of filters and impactors, they all still share common drawbacks, namely, the need for long sampling periods, which precludes the observation of short time chemical changes in air masses, and the use of subsequent off-line analysis methods, which suffer from disadvantages such as possible contamination from analytical procedures and sample handling, time consumption, and potential decomposition of labile compounds during analysis. Consequently, research into on-line aerosol measurements has been an important step forward. Some of these methods will now be considered.

2.4.2 On-line methods

In-situ monitoring methods for the analysis of aerosol chemical composition increase sample frequency and decrease operating costs. They have great potential to reduce particle volatilisation because environmental variables such as temperature and relative humidity do not normally fluctuate over sub-hourly sample durations and because sample transport and storage is unnecessary. These methods automate the collection and analysis steps in order to overcome the problems related to the off-line techniques (see

section 2.4.1). The feasibility of using automated analysers for measuring sulphate, nitrate, elemental carbon, and organic carbon has been demonstrated.

The Aethalometer is a soot monitor that measures the concentration of black carbon (BC) in ambient air based on the light absorption in filter samples [*Hansen et al., 1984*]. The difference in attenuation between exposed and blank filters is proportional to the amount of light-absorbing carbonaceous aerosol captured. Because carbonaceous aerosol contains a mixture of hundreds of compounds, it is usually reported simply as total carbon and often fractionated into organic carbon (OC) and elemental carbon (EC). For determination of OC/EC, in-situ thermal/optical analysers have been developed (e.g. the thermo-optical analyser, Sunset Laboratories, Forest Grove, OR, USA). The basic premise of these thermal methods is that organic carbon is volatilised from a sample when heated in the absence of oxygen, whereas oxygen is required for the combustion of elemental carbon [*Turpin et al., 1990; Chow et al., 1993; Grosjean et al., 1994*]. Total carbon is the sum of OC and EC. In a typical thermal analysis method, the sample is heated in a temperature-programmed chamber in the presence of one or more gases. OC is identified by its evolution under a heating cycle in the presence of either He or N_2. EC is defined as the fraction that subsequently evolves in a gas mixture containing mainly oxygen. The evolved carbon passes over a catalyst converting the gases to CH_4 or CO_2, which is subsequently quantified by an IR or a flame ionisation detector (FID). Some organic carbon compounds pyrolyse before they evolve under the He/O_2 segment of the analysis. If not accounted for, this can result in an overestimation of the elemental carbon fraction. The lack of standards for OC/EC analysis suitable for ambient measurements is a disadvantage of these methods. In a comparative study on aerosol samples [*Turpin et al., 1990*], the quantification of OC and EC has shown great variability on similar samples because of the different protocols used. Thus, unless the same protocol is applied for OC/EC determination, measurements from different studies and different sources are not comparable.

This type of analysis measures the mass of carbon in organics rather than the mass of organic compounds (i.e., it does not include the contribution of other elements such as O, H, and N present in the organic compound). A multiplicative factor of 1.2 or 1.4 is

commonly used to estimate the organic compound mass concentration from the measured organic carbon content [*Gray et al., 1986*]. This factor is an estimate of the average molecular weight of organic compounds per gram of organic carbon in atmospheric particle samples measured in a few urban locations in the 1970s [*Grosjean and Friedlander, 1975*]. *Turpin and Lim* [*2001*] have recently examined the accuracy of the 1.4 factor in non-urban areas and found that values of 1.3 and 3.2 more accurately described the average molecular weight per carbon weight for "water-insoluble" and "water-soluble" organic compounds, respectively. Their work suggested that while 1.4 is a reasonable factor for urban aerosol, a ratio of 1.9-2.3 is more accurate for an aged aerosol, and 2.2-2.6 better represents an aerosol heavily influenced by wood smoke.

Several groups have developed techniques for in-situ measurements of particulate sulphate concentrations utilising flame photometric detectors (FPD) [*Huntzicker et al., 1978; Kittelson et al., 1978*]. The FPD detects ~ 394 nm light given off by excited-state S_2 molecules formed when sulphur compounds are burned in a hydrogen-rich flame. This method does not distinguish between gaseous and particulate sulphur, therefore a denuder is typically used to remove the interfering gases before they enter the hydrogen-rich flame. Measurements of sulphate speciation with the FPD have been reported. Speciation is achieved by heating the aerosol to various temperatures upstream of the particle sulphur monitor. Studies have shown that temperatures of 71, 142, and 190 ^{o}C, respectively volatilise sulphuric acid, ammonium sulphate and refractory sulphur species [*Huntzicker et al., 1978; Kittelson et al., 1978*]. A system for measuring particulate nitrate concentrations has been developed [*Stolzenburg and Hering, 2000*]. The sampled aerosol is humidified to prevent bounce during particle collection by impaction. Collected particles are converted to gas phase NO_x using flash vaporisation, which is then analysed by a chemilluminescent NO_x analyser. Inductively coupled plasma (ICP) seems to be the most well developed technique at present for real-time measurements of particulate metal concentrations in ambient air [*Spurny, 1999*].

While these methods offer a higher time resolution compared to the off-line methods (minutes are possible), they do not provide size-resolved data and are limited to one aspect of the aerosol chemistry. Recently, systems have been reported to measure multi-

component aerosols. These new systems utilise mainly ion chromatography (IC) techniques for chemical analysis and use particle collection systems, mainly denuders, to remove gases. The particle into liquid sampler (PILS) [*Weber et al., 2001; Orsini et al., 2003*] measures several ions in particulate matter. Ambient particles are grown to large sizes in a saturated water vapour environment and are collected on a surface that is continually flushed with water. The liquid sample is then injected into a dual-channel IC for analysis of anions and cations. Measurements of aerosol components such as nitrate, sulphate, chloride, ammonium, sodium, calcium and potassium have been reported at high time resolution (minutes). The drawback of this technique, in addition to the lack of size discrimination of particle composition, is that it is only suitable for particles that will act as water condensation nuclei. Because these approaches are amenable to the simultaneous measurement of semivolatile gases and particulate species, they provide information on a number of species at relatively high time resolution for typical ambient concentrations, and so they show promise for the future.

The breakthrough of on-line aerosol analysis happened with the introduction of aerosol mass spectrometers. According to *McMurry* [*2000*] "*these mass spectrometers are, arguably, the most significant development in aerosol measurement in the past 20 years and show great promise for providing rich new insights into sources and chemical transformations of atmospheric aerosols*". These methods are discussed in detail and reviewed in section 2.6 of this chapter.

2.5 Measurements of other aerosol properties

Electron microscopy techniques can be used to provide information on the morphology of individual particles. With this approach, particles are collected on a filter or by impaction onto substrates and are then magnified and imaged by electron beams under vacuum conditions. The measurement of particles containing volatile species (e.g. nitrates and semivolatile organic compounds) by electron microscopy can be problematic. Volatilisation occurs because particles are exposed to vacuum conditions for extended times during analysis and because samples are heated by the electron beam [*Almasi et al., 1965*]. The environmental scanning electron microscope (ESEM) [*Danilatos and Postle, 1982; Danilatos, 1988*] permits the analysis of particles exposed

to gas pressures exceeding 5 torr, thereby eliminating some of the volatilisation losses that occur in the conventional electron microscopes.

Measuring the bulk optical properties of ambient particles is of much interest, as these dictate what direct effect they will have on the Earth's climate (see section 1.1.2.2). Integrating nephelometers (e.g. TSI model 3563) measure the total amount of light scattered by an aerosol. The "integration" covers scattering angles from near forward to near backward directions. The design and applications of the integrating nephelometer have been reviewed by *Heintzenberg and Charlson* [*1996*].

The ability of atmospheric aerosols to absorb water and grow in size with increasing relative humidity influences their light scattering and cloud condensation nuclei properties. The hygroscopic behaviour of aerosols can influence their direct and indirect effects on global climate. This behaviour is also important for determining the impacts of aerosol on human health when particles are breathed into the water-saturated environment of the lung. The hygroscopicity tandem differential mobility analyser (HTDMA) is an increasingly common instrument for investigating the particle behaviour in subsaturated humidities [*Rader and McMurry, 1986*]. This instrument involves the use of two DMAs operated in series. The first DMA selects particles of a known 'dry' size, which are then passed into a humidifier. The second DMA is then scanned to provide a 'wet' size distribution of the humidified selected 'dry' size. Particles may take on water and have different growth factors during humidification depending on their size and chemical composition. The presence of more than one mode in the 'wet' size distribution is an indication of externally mixed particles within the selected 'dry' size. However, organic particles take some time to reach equilibrium when exposed to a change in humidity and when they are measured using such techniques may not have reached their equilibrium diameter.

In addition to the humidification of particles, other conditioning techniques have been employed with TDMA systems in order to study various aspects of particle composition. For example, organic solvents (e.g. propanol), as opposed to water, have been used to grow particles in the organic TDMA (OTDMA) [*Joutsensaari et al.,*

2001]. Heating particles of a selected size at high temperatures (>100 ^{o}C) has been undertaken in the volatility TDMA (VTDMA) [*Orsini et al., 1999; Schmid et al., 2002*]. Some results obtained with the latter instrument are discussed in chapter 6.

The ability of aerosol particles to act as cloud condensation nuclei is an important property, which can alter the microphysical properties of clouds that subsequently form on them. This can, in turn affect the global climate (see section 1.1.2.2). In order to develop valid models for such phenomena, it is necessary to understand the relationship between atmospheric aerosol properties and the number and size of cloud droplets that can be produced from them. Cloud condensation nuclei (CCN, e.g. Droplet Measurement Technologies Inc., Boulder, CO, USA) counters measure the concentration of particles that are converted to cloud droplets by condensation of water (i.e. "activated") at a specified value or range of values of supersaturation [*Junge and McLaren, 1971; Fitzgerald, 1973*]. Unlike condensation particle counters (CPCs), which use a variety of working fluids at supersaturations of several hundred percent, CCN counters use only water and operate at supersaturations pertinent to cloud formation (typically 0.01 to 1%). Therefore, the CCN concentration is a fraction of the total particle number measured by CPCs and depends on the supersaturation employed. Most CCN instruments use thermal gradient diffusion chambers to produce the desired supersaturations. For a review of the design and applications of CCN instruments the reader is directed to *McMurry* [*2000*].

2.6 On-line aerosol mass spectrometry

While aerosol scientists have developed a large number of techniques for measuring the physical properties of aerosols, it is now understood that future progress in understanding aerosol properties, processes and impact will require the development of new techniques for particle chemical analysis, which are also capable of determining the size, shape, optical properties and elemental and molecular composition of each particle in real time. Over the past decade or so, aerosol mass spectrometry has gained considerable interest as a means of correlating the size and chemical composition of individual particles in real-time. This approach involves drawing an aerosol directly into a mass spectrometer where individual particles are analysed within a few milliseconds

of entering the vacuum. Sampling artefacts are greatly reduced and the time required to characterise the aerosol is limited only by the amount of time needed to analyse a statistically significant number of particles, typically a few minutes. While a large number of techniques and principles have been implemented in the development of various aerosol mass spectrometers, the basic concepts of the operation of these instruments may be classified into several discrete stages which include: sample introduction, aerosol sizing techniques, vaporisation methods, ionisation techniques, and mass spectrometer types. This section discusses the basic principles of these analytical tools and attempts to review some of the major key steps in their development. A more comprehensive history and reviews of the individual aerosol mass spectrometers are available elsewhere [*Suess and Prather, 1999; Johnston, 2000; Noble and Prather, 2000; Sipin et al., 2003*].

2.6.1 Inlet technology

The first crucial step in aerosol measurement and analysis is to obtain a representative particulate sample. Methods have to be applied that do not disturb the dynamics of the aerosol sample and do not change the physical and chemical state of single particles. Contamination and alteration, such as volatilisation or crystallisation, of substances are possible and can lead to false conclusions about original particles. There have been major advances in this area ranging from the physical placement of the sample into the ionisation region of the mass spectrometer to introducing ambient particles on-line into the mass spectrometer [*Spurny, 1999; Suess and Prather, 1999; Johnston, 2000*]. A variety of inlets has been utilised to draw particles from atmospheric pressure into the vacuum chambers of the aerosol mass spectrometers, including nozzle [*Reilly et al., 2000; Trimborn et al., 2000*], capillary [*Reents and Schabel, 2001*] and aerodynamic lens systems [*Jayne et al., 2000; Tobias et al., 2000*]. In each case, the gas emerging from the inlet undergoes a supersonic expansion into a vacuum. Because of their greater mass, particles deviate from the streamlines of the expanding gas and form a particle beam.

Understanding the characteristics of the particle beam emerging from the various inlets is very important as it forms the basis for particle introduction into most of the modern

aerosol mass spectrometers [*Liu et al., 1995a; Liu et al., 1995b; Johnston, 2000*]. The single particle velocity within this beam depends greatly upon the particle's size, shape, and density with larger more massive particles travelling at slower velocities than smaller particles. Divergence is also an important characteristic of particle beams in which smaller particles follow gas flow more than particles with greater mass. This leads to a greater beam divergence for smaller particles. Capillaries are frequently used for sampling particles at the lower end of the coarse mode and the high end of the accumulation mode and have been shown to be able to transmit a wider range of particle sizes more efficiently than nozzles [*Mallina et al., 1999; Johnston, 2000*]. More recently, aerodynamic lenses have been employed in aerosol mass spectrometers, allowing for much greater transmission efficiency of smaller particles into the ion source region. The latter system is described in more detail in the next chapter (see section 3.1.1).

2.6.2 Particle sizing techniques

After a particle beam is formed, there are two main possible ways to obtain particle size information. These include measuring the light scattering intensity from particles as they pass through a single laser (optical particle sizing) [*Murphy and Thomson, 1995*], or measuring the particle time-of-flight between two fixed points (aerodynamic particle sizing) [*Prather et al., 1994; Gard et al., 1997; Jayne et al., 2000*]. In the later case particles are mainly detected using lasers, although other detection techniques have been used (see chapter 3, sections 3.1.2 and 3.2.2). In either case, the scattered light intensity or the flight time can be related to particle size upon system calibration using particles of known sizes [*Salt et al., 1996; Jayne et al., 2000*].

Aerodynamic particles sizing is preferred over the light scattering method because it allows for a more accurate determination of particle size and offers higher size resolution and a lower size limit of detection. *Salt et al.*, [*1996*] compared the sizing results of monodisperse particles of known chemical composition (sodium chloride or 2,4-dihydroxybenzoic acid) using both methods and found that determining particle size using single laser light scattering intensity collected at a single angle results in broad standard deviations. These deviations were explained by the complex dependence of

scattered light intensity from a single particle on particle size, shape, refractive index, and wavelength of the incident radiation. The scattering intensity was also found to be partially affected by each particle's trajectory through the scattering laser beam profile. These problems are expected to be amplified when sizing ambient aerosol particles, which contain many more sizes and have a more complex chemical composition. In contrast, aerodynamic sizing measurements produced relatively small standard deviations, permitting determination of the aerodynamic size of single particles in a polydisperse aerosol sample.

2.6.3 Mass spectrometry

During the development of aerosol mass spectrometers, different types of mass spectrometers, or mass analysers, have been utilised including magnetic sector, ion trap, time-of-flight, and quadrupole instruments. The principle difference among these analysers lies in their systems for separating ions. A brief description of each system is provided in this section. *Magnetic sector mass spectrometers* apply a magnetic field that separate ions into discrete packets according to their mass-to-charge ratio (*m/z*). These ion packets travel on slightly different trajectories through the instrument and are detected upon their exit from the magnet. The trajectory of ions in a magnetic sector mass spectrometer is determined by the following equation [*Rose and Johnstone, 1982*]:

$$\frac{m}{z} = \frac{B^2 r^2 e}{2V} \tag{2.1}$$

where *m/z* is the mass-to-charge ratio, B is the magnetic field strength, r is the curvature radius of the magnetic sector, e is the charge of an ion, and V is the acceleration voltage. In most cases, a magnetic sector instrument is used in conjunction with an electrostatic analyser and is referred to as a double focusing MS. The electrostatic analyser is used to account for the different kinetic energies resulting from ion formation. A mass spectrum is obtained by either scanning the magnetic field strength or the acceleration voltage while holding the other parameters constant. Magnetic sector instruments were utilised in the early stages of aerosol mass spectrometry development [*Davis, 1973*], but their use in portable instruments has been limited by their large sizes. In addition, the

scanning nature of these instruments, a complete mass spectrum cannot be obtained from a single particle, prevented their implementation in single particle mass spectrometers [*Suess and Prather, 1999*].

Quadrupole mass spectrometers (QMS), Figure 2.2, employ four parallel, cylindrical metal rods arranged symmetrically around the ion beam, which is accelerated using an electric field. The two sets of opposing rods possess either a variable positive or negative DC potential. In addition, variable radio-frequency AC potentials are applied 180 degrees out of phase to these same rods. The ions adopt oscillating trajectories as they travel between the rods; the magnitude of the oscillations being determined by their mass-to-charge (*m/z*) ratios, the applied AC and DC voltages and the frequency of the AC voltage. Typically, the frequency is kept constant during operation, since it is simpler to alter the magnitude of the voltages. The combined fields cause the ions to oscillate about their central axis of travel; only those with a certain mass-to-charge (*m/z*) ratio can pass through the array without being removed by collision with one of the rods [*Rose and Johnstone, 1982*]. Mass spectra are obtained by scanning the *m/z* range of interest by varying the AC and DC potentials while keeping their ratio and also the frequency constant. Similar to magnetic sector mass spectrometers quadrupoles cannot be used to obtain a complete mass spectrum for single particle analysis as the time needed to scan the full mass range is too long. However, quadrupoles are much more compact, robust and generally simpler to implement than many other mass spectrometers, making them ideal for field instrumentation.
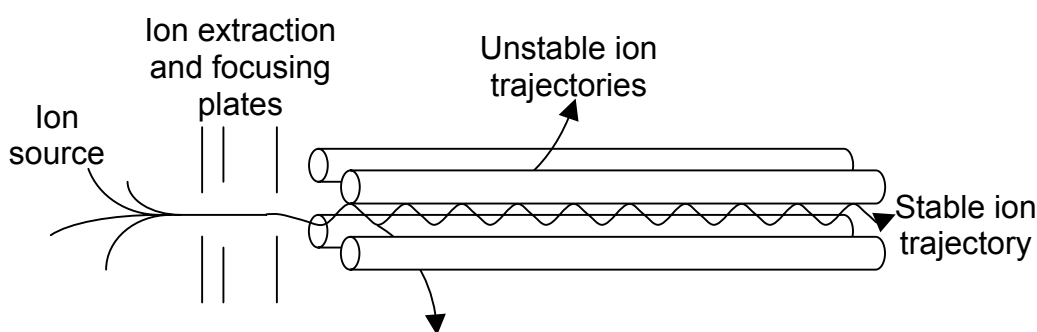

Figure 2.2: A basic schematic illustrating the principles of a quadrupole mass spectrometer

Time-of-flight mass spectrometers (TOFMS) are based on mass analysis of ions by flight times. Ideally, after ionisation all ions have the same kinetic energy. Hence, ions of smaller mass will reach the detector with shorter flight times than larger ions. TOFMS is based on the following equation [*Rose and Johnstone, 1982; Suess and Prather, 1999*]:

$$ t \; = \; L \left(\frac{m}{2 \, ezV} \right)^{1/2} \tag{2.1} $$

where *m/z* is the mass-to-charge ratio of the ion, V is the ion's acceleration voltage, t is the ion's flight time, e is the electronic charge and L is the length of the flight tube. This type of mass spectrometer has the major advantage of being able to simultaneously detect ions of many *m/z*, which is not possible with the previous two methods. However, pulses of ions must be created in the ionisation region of TOF systems, as sampling a continuous ion stream is not possible with this type of mass spectrometers. Laser-based ionisation on single particles offers such a pulsed ion source and as a result TOFMS have been widely utilised in modern aerosol mass spectrometers designed for single particle analysis [*Suess and Prather, 1999; Johnston, 2000*].

Finally, *Ion trap mass spectrometers* (ITMS) consist of a doughnut-shaped ring electrode and two end cap electrodes that are usually at ground. Ions are trapped when a variable radio frequency (RF) voltage is applied to the ring electrode. As the RF amplitude increases, larger ion orbits stabilise while smaller ions destabilise and collide with the ring electrode. All ions within a designated *m/z* range can be trapped, and a complete mass spectrum can be taken by ramping up the RF voltage. As the ion orbits destabilise, they are ejected through an opening in an end cap and detected usually by an electron multiplier. Like the TOFMS, it is possible with this technique to obtain a complete mass spectrum from a single ionisation event. Also, it has a higher resolution compared to QMS because the ions spend a longer time between the electrodes. ITMS has the ability to trap one specific *m/z*, where tandem MS/MS can be accomplished. This is a valuable tool for gaining additional chemical information and interpreting mass spectra [*Yang et al., 1996*].

2.6.4 Thermal-based aerosol mass spectrometry

Davis [*1973*] developed the first on-line aerosol mass spectrometer, in which particles were analysed by a surface ionisation magnetic sector mass spectrometer. Aerosol particles were introduced into the instrument through a steel capillary and thin wall pinhole. Upon impaction on a surface (either rhenium or tungsten) heated up to 1700 ^{o}C, aerosol particles evaporated and resulted in neutral and ionic species. During the 1970s, other surface ionisation instruments were developed, some utilised quadrupole mass spectrometers instead of magnetic sector instruments [*Myers and Fite, 1975*]. The surface ionisation method was limited only to species with ionisation potentials below the work function of the heated surface (~ 8 eV), typically alkali and alkaline earth metals. Interactions between the heated surface and particle components were also possible. These problems were overcome by separating the vaporisation and ionisation steps in instruments such as the Chemical Analysis of Aerosol in Real Time (CAART) [*Allen and Gould, 1981*] and the Particle Analysis by quadrupole Mass Spectrometry (PAMS) [*Sinha et al., 1982*]. In these instruments, particles were vaporised into a neutral gas by impaction on a heated surface before being ionised using electron impact (EI). Electron impact ionisation happens when a highly energetic electron beam emitted by a heated filament is directed towards gaseous analyte molecules present in the ionisation region of a mass spectrometer. The energy of the electron beam is usually much higher than the ionisation potential of the analyte molecules, leading to a high degree of molecular fragmentation. Normally, EI utilises electrons with 70 eV kinetic energy and standard libraries of mass spectra of organic compounds obtained with this method are available (e.g. http://webbook.nist.gov).

More recently, the Thermal Desorption Particle Beam Mass Spectrometer (TDPBMS) has been developed to investigate secondary organic aerosols formation [*Tobias and Ziemann, 1999; Tobias et al., 2000*]. This instrument is based on the same basic principles introduced earlier [*Allen and Gould, 1981; Sinha et al., 1982*]. However, to separate complex mixtures, particles are impacted onto a cryogenically cooled metal foil that is slowly heated to separate components based on their vapour pressure. This technique offers a time resolution superior to traditional GC methods. Furthermore, thermal decomposition is less likely since vaporisation occurs quickly and at lower

temperatures under vacuum. The technique has been shown to be a powerful tool for organic aerosol analysis, as mass spectral data as a function of chemical volatility can be obtained and linked to the vapour pressure, molecular weight and functional group composition of the parent species. The TDPBMS has been used to observe secondary aerosol formation from the ozonolysis of volatile organic species [*Tobias and Ziemann, 2000; Ziemann, 2002*]. It has also been used to identify products from diesel exhaust, where results showed that the majority of the organic carbon in particles produced from diesel engines was due to lubricating oil, and not from the incomplete combustion of fuel [*Tobias et al., 2001; Sakurai et al., 2003*].

In addition to electron impact ionisation and quadrupole mass spectrometry, other techniques have been utilised in thermal-based aerosol mass spectrometers. 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 being analysed through processes such as proton transfer. An ion trap mass spectrometer is used to analyse the resultant ions. This technique has been primarily designed to investigate gas-phase organic species, but a denuder can be used to remove these prior to analysis and the aerosol particles can be thermally vaporised and studied in the same way. This is a "softer" ionisation process that results in less fragmentation of the parent molecules compared to EI, and therefore it is especially useful for the identification and quantification of organic compounds [*Kuckelmann et al., 2000*]. However, as a result of the selective nature of the ionisation process, not all the particulate mass will be analysed.

Although the thermal-based aerosol mass spectrometers have provided valuable information on the chemical composition of aerosol particles, they do have a number of intrinsic problems. The use of magnetic sector and quadrupole mass spectrometers means that these instruments are only capable of studying one m/z at a time, and therefore only one aspect of the chemical composition of a single particle can be investigated. While ion trap mass spectrometers can scan multiple values of m/z, thermal vaporisation processes are not fast enough to study individual particles. As a

result, these instruments can provide information on the chemical composition of an ensemble of particles or on a single component of individual particles, but they are not suitable for single particle analysis and cannot provide direct information on the mixing states of aerosol particles. Thermal vaporisation methods are limited by the volatility of the chemical components of the aerosol particles under analysis. While volatile and semivolatile aerosol components (e.g. ammonium nitrate, ammonium sulphate, organic compounds) can be readily vaporised upon impaction on heated surfaces, refractory substances such elemental carbon and crustal material do not usually volatilise at the operating temperatures of these surfaces (typically < 650 ^{o}C). As a result, these instruments are not suitable for the analysis of such aerosol components. Finally, the instruments discussed so far have no direct method of measuring the size of the particles being analysed. For example, a DMA was used in series with the TDPBMS to study the chemical composition of particles of a known size. However, in order to obtain size-resolved chemical information, several DMA sizes must be selected consecutively. This will require an extended period of time to obtain a complete scan and will result in a relatively poor time-resolution, which is not desirable for ambient data measurements. Much of the effort in the area of aerosol mass spectrometry has been concentrated over the past decade or so on the development of laser-based instrumentation to address these issues.

2.6.5 Laser-based aerosol mass spectrometry

The main feature of this type of instrumentation is the use of a single short laser pulse for both particle desorption and ionisation. The most common types of laser, which have been utilised in this technique include excimer, neodymium-yttrium aluminium garnet (Nd:YAG), and CO_2 lasers at different wavelengths. The laser desorption ionisation (LDI) technique and a highly improved method for particle sizing were first combined for aerosol composition analysis by *Sinha* [*1984*]. The instrument consisted of a particle sizing region and a mass spectrometer for ion monitoring. Two continuous wave He:Ne lasers, located at a known distance apart were used to measure particle velocities. A calibration curve of aerodynamic particle diameter versus particle velocity was then used to determine particle size. A third laser, a high-energy pulsed Nd:YAG,

was then used for the desorption and ionisation of each particle and the ions produced were analysed by a quadrupole mass spectrometer.

The breakthrough in single particle analysis occurred when *McKeown et al.*, [*1991*] coupled the LDI technique to a time-of-flight aerosol mass spectrometer. The major advantage of combining LDI and TOFMS is the fact that, unlike quadrupole and magnetic sector methods, TOFMS has the ability to obtain an entire spectrum on the order of microseconds while also having a theoretically unlimited mass range, making it ideal for single particle analysis, especially when pulsed ion sources such as lasers are used. In addition, LDI is a fast and highly efficient vaporisation and ionisation technique that requires no sample preparation. Several instruments have been developed based on the combination of LDI and TOFMS. Comprehensive reviews of the history and the principles and techniques applied in these instruments are available elsewhere [*Suess and Prather, 1999; Johnston, 2000; Noble and Prather, 2000; Sipin et al., 2003*]. Examples of these instruments include Laser Mass analysis of Particles in the Airborne State (LAMPAS) [*Hinz et al., 1994; Hinz et al., 1996*], Particle Analysis by Laser Mass Spectrometry (PALMS) [*Murphy and Thomson, 1995; Thomson et al., 2000*], Rapid Single-particle Mass Spectrometry (RSMS) [*Carson et al., 1995*], the Particle Blaster [*Reents et al., 1995*], Aerosol Mass Spectrometry (AMS) [*Hunt and Petrucci, 2002*], and the Aerosol Time Of Flight Mass Spectrometer (ATOFMS) [*Prather et al., 1994; Gard et al., 1997*]. The latter instrument is commercially available from TSI Inc. as the ATOFMS model 3800. A schematic diagram of this instrument is shown in Figure 2.3. Most of the successful ideas, which have over the years been introduced into the field of aerosol mass spectrometry, have been implemented in the ATOFMS. The instrument employs dual laser system for aerodynamic particle sizing [*Sinha, 1984*], a dual polarity TOF mass spectrometer for the simultaneous analysis of both positive and negative ions [*Hinz et al., 1996*], and it uses reflectrons to improve the resolution of the TOFMS [*Carson et al., 1995*]. More recently, TSI have started manufacturing an aerodynamic lens (model 3801-030) as an accessory for the ATOFMS.

The use of LDI has not been limited to TOF mass spectrometry. For example a laser-based instrument that utilises an ion trap mass spectrometer has been presented [*Yang et*

al., 1996; Reilly et al., 1997]. This instrument has been used to perform tandem mass spectrometry (MS/MS), where ions of a single *m/z* are fragmented further and studied in more detail, providing additional chemical information and a powerful means for the identification of organic compounds.
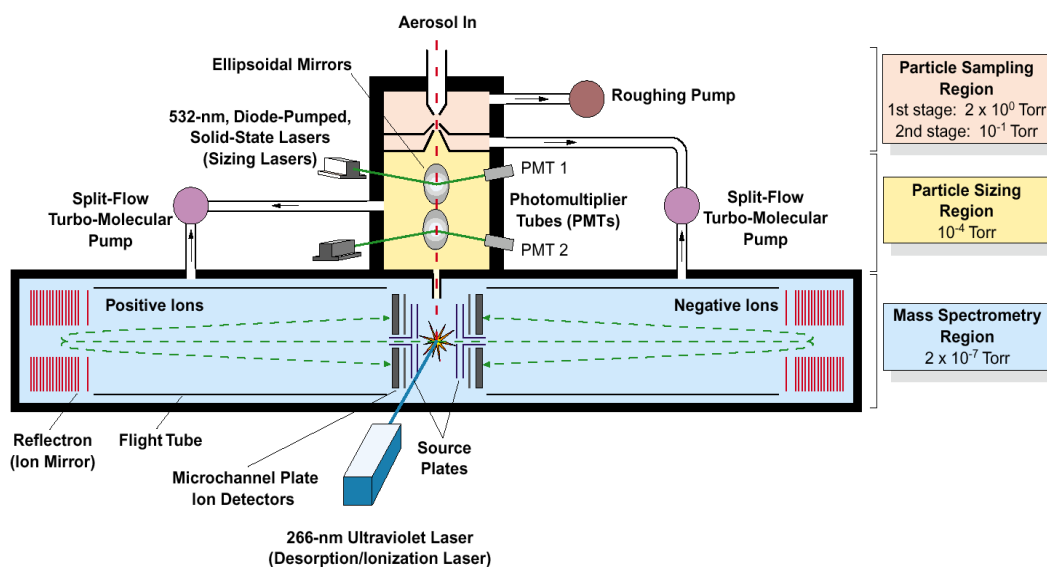

Figure 2.3: A schematic diagram of the commercially available Aerosol Time Of Flight Mass Spectrometer (ATOFMS), TSI Model 3800

Laser-based aerosol mass spectrometers are proving to be powerful and unique tools with a large number of applications [*Suess and Prather, 1999*]. Besides their ability to provide valuable information on the chemical associations in single-particles (i.e. mixing states), these techniques allow the analysis of inorganic, organic, thermally labile, or relatively non-volatile substances with a high time resolution. For example they can provide information on the presence of aerosol components such as organic carbon, elemental carbon, sulphates, nitrates, sea salt, dust and metals. As a result, their application for the characterisation of atmospheric particles has increased in recent years [*Silva and Prather, 1997; Middlebrook et al., 1998; Murphy et al., 1998; Lazar et al., 2000; Liu et al., 2000; Lee et al., 2002; Warscheid and Hoffmann, 2002; Lee et al., 2003; Beddows et al., 2004; Dall'Osto et al., 2004; Tolocka et al., 2004c; Tolocka et al., 2004b*]. A major strength of laser-based instruments lies in their ability to track and identify particles from various sources in the atmosphere [*Silva and Prather, 2000; Bhave et al., 2001*]. These instruments normally produce very large data volumes during

ambient sampling because individual mass spectra for hundreds of thousands of particles are routinely recorded. The development of analysis tools for these data sets is currently an active area of research, where most of the available tools are based on grouping particle mass spectra according to common features and relating them to the aerosol chemical composition and sources [*Song et al., 1999; Phares et al., 2001; Murphy et al., 2003*].

While qualitative information on the chemical composition of aerosol can be obtained, providing quantitative data with LDI represents an intrinsic problem. LDI methods that employ high laser fluence (energy of pulse) can produce extensive fragmentation of molecules and quantitative data on elementary composition can be obtained [*Reents and Schabel, 2001*], although information on molecular structure cannot be retrieved. Less fragmentation occurs at lower fluences, allowing more chemical information to be obtained, but at the same time, the particle components are not necessarily fully vaporised by the laser pulse and are therefore detected with varying efficiency depending on the particle's size and chemical composition. Furthermore, incomplete vaporisation makes ionisation more sensitive to species present on the surface than those in the core [*Allen et al., 2000; Kane and Johnston, 2000*]. Shot-to-shot variations in laser power density and beam profile inhomogeneities can be dramatic, making signal quantification with LDI even more challenging. In addition, individual chemical components can interact with each other during the combined desorption and ionisation processes, resulting in an uneven distribution of charges between the fragments. The causes of this are known as 'matrix effect' [*Reilly et al., 2000*]. It is also important to understand that spectral intensities depend not only on the laser power density absorbed by the molecules, but also on the instrument sensitivity to the specific species, which depends on the absorption characteristics of the individual species present in the sample under study [*Gross et al., 2000*].

The other difficulty with LDI is the qualitative identification of organic compounds in single particles. The speciation of organic compounds is difficult with this technique due to the extensive fragmentation caused by the high-energy, multiphoton ionisation process. LDI mass spectra in many cases produce different fragmentation patterns when

compared with other ionisation techniques such as EI. This can make qualitative identification of chemical species difficult to achieve, especially with the lack of standard libraries of mass spectra such as those available for EI. Also, aliphatic compounds and their derivatives are routinely not detected with LDI, as the presence of a functional group is often required to either absorb the laser photons or obtain a charge [*Silva and Prather, 2000*].

Several approaches have been taken to improve the quantification abilities of these laser-based methods including ensemble averaging [*Reents and Ge, 2000; Reents and Schabel, 2001*], and evaluation of relative response factors [*Gross et al., 2000; Reilly et al., 2000*]. However, the introduction of the two-step laser method appears to produce promising results. This method decouples the desorption and ionisation processes by using two separate, weaker lasers, thus allowing independent optimisation of each process [*Morrical et al., 1998*]. This technique has been further investigated, improved and implemented by another research group [*Cabalo et al., 2000*]. Particles are focused into a narrow beam and aerodynamically sized by measuring their time of flight between two continuous wave lasers separated by a known distance. The speed of the particle determines the time when a tunable CO_2 laser (desorption) and subsequently an excimer laser (ionisation) fire, and the analysis is followed by time-of-flight mass spectrometry. This system was further improved by using a vacuum UV radiation for the ionisation step in order to carry out single-photon ionisation, demonstrating the ability for quantification of polycyclic aromatic hydrocarbons (PAHs) while gaining molecular ion information [*Woods et al., 2001*]. Since dimensions of CO_2 lasers can be quite large for field applications, replacement of this laser with thermal desorption has been introduced as an alternative for portable instruments [*Sykes et al., 2002*]. For this purpose, a cartridge heater is inserted between the ion extraction plates and particles are vaporised at 500 – 700 K followed by VUV ionisation. However, like thermal-based instruments, elemental carbon, sea salt and dust are not vaporised, making their determination not possible. The suggested design of the latter instrument, and the review of the thermal- and laser-based aerosol mass spectrometry methods presented in this chapter, demonstrate the complementary nature of these instruments and that a 'perfect' single instrument is not yet available.