

Chapter 17

A review of atmospheric aerosol measurements

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Abstract

Recent developments in atmospheric aerosol measurements are reviewed. The topics included complement those covered in the recent review by Chow (JAWMA 45: 320–382, 1995) which focuses on regulatory compliance measurements and filter measurements of particulate composition. This review focuses on measurements of aerosol integral properties (total number concentration, CCN concentration, optical coefficients, etc.), aerosol physical chemical properties (density, refractive index, equilibrium water content, etc.), measurements of aerosol size distributions, and measurements of size-resolved aerosol composition. Such measurements play an essential role in studies of secondary aerosol formation by atmospheric chemical transformations and enable one to quantify the contributions of various species to effects including light scattering/absorption, health effects, dry deposition, etc. Aerosol measurement evolved from an art to a science in the 1970s following the development of instrumentation to generate monodisperse calibration aerosols of known size, composition, and concentration. While such calibration tools permit precise assessments of instrument responses to known laboratory-generated aerosols, unquantifiable uncertainties remain even when carefully calibrated instruments are used for atmospheric measurements. This is because instrument responses typically depend on aerosol properties including composition, shape, density, etc., which, for atmospheric aerosols, may vary from particle-to-particle and are often unknown. More effort needs to be made to quantify measurement accuracies that can be achieved for realistic atmospheric sampling scenarios. The measurement of organic species in atmospheric particles requires substantial development. Atmospheric aerosols typically include hundreds of organic compounds, and only a small fraction (~10%) of these can be identified by state-of-the-art analytical methodologies. Even the measurement of the total particulate organic carbon mass concentration is beset by difficulties including the unknown extent

of evaporative losses during sampling, adsorption of gas-phase organic compounds onto sampling substrates, and the unknown relationship between carbon mass and mass of the particulate organics. The development of improved methodologies for such measurements should be a high priority for the future. Mass spectrometers that measure the composition of individual particles have recently been developed. It is not clear that these instruments will provide quantitative information on species mass concentrations, and more work is needed to routinely interpret the vast quantities of data generated during field sampling. Nevertheless, these instruments substantially expand the range of atmospheric aerosol issues that can be explored experimentally. These instruments represent the most significant advance in aerosol instrumentation in recent years.

1. Introduction

Atmospheric aerosol particles range in size over more than four orders of magnitude, from freshly nucleated clusters containing a few molecules to cloud droplets and crustal dust particles up to tens of microns in size. Average particle compositions vary with size, time, and location, and the bulk compositions of individual particles of a given size also vary significantly, reflecting the particles' diverse origins and atmospheric processing. Particle surface composition is also an important characteristic since it affects interfacial mass transfer and surface reactions, which play a role in atmospheric chemical transformations. Such transformations can be significant both for their effects on gas-phase composition, as in stratospheric ozone depletion, and for their effects on particle composition. The production of fine (sub 2.5 μm) sulfates by liquid transformations in clouds is an example of a process that involves gas-to-particle mass transfer of species including water, sulfur dioxide, and oxidants.

An aerosol is defined as a suspension of liquid or solid particles in a gas. In reviewing aerosol measurement it is important to remember the gas. While atmospheric particles contain nonvolatile species such as salt, soot, metals, and crustal oxides, they also contain semivolatile compounds such as nitrates and many organic compounds. The distribution of such semivolatile compounds between the gas and particle phases varies with the amount of available particulate matter on which they can accumulate, the thermodynamic properties of the semivolatile compounds, and the gas and particle composition. Furthermore, fine (<2.5 μm) atmospheric particles are mostly hygroscopic and the water mass fraction in the condensed phase increases with relative humidity. Water typically constitutes more than half of the atmospheric fine particle mass at relative humidities exceeding roughly 80%. Thus, particle composition is inextricably linked with the composition of the gas phase, adding to the challenge of adequately characterizing the aerosol. Furthermore, sampling and/or

measurement can change the thermodynamic environment or gas-phase composition thereby causing changes in particle composition before measurements are carried out.

In his visionary articles Friedlander (1970,1971) introduced a conceptual framework for characterizing instruments used for aerosol measurement. In these articles, he defined the aerosol size-composition probability density function $g(v, n_1, \dots, n_{k-1})$ for an aerosol containing k chemical species. This function is defined such that the fraction of the total number concentration N_∞ having particle volume between v and $v + dv$, and molar composition of species i between n_i and $n_i + dn_i$ at time t is

$$\frac{dN}{N_\infty} = g(t, v, n_1, \dots, n_{k-1}) dv dn_1 \dots dn_{k-1}. \quad (1)$$

Only $k - 1$ species are specified as independent variables because particle volume depends on the species' molar composition:

$$v = \sum_{i=1}^k n_i \bar{v}_i, \quad (2)$$

where $\bar{v}_i$ is the partial molar volume of species i . This formulation does not explicitly account for particle charge states, surface composition, morphologies, phase composition, etc., but it could in principle be generalized to include such information. Gas-phase compositions are implicitly coupled through the dependence of particle composition n_i on the gas phase.

Knowledge of $N_\infty g(t, v, n_1, \dots, n_{k-1})$ would provide a comprehensive characterization of the size-resolved aerosol composition, including variations in composition among particles of a given size. Advances in single-particle mass spectrometry during the past several years have moved us closer to making such information a reality. Most aerosol measurements, however, provide integrals over time, size, and/or composition.

Fig. 1, adapted from Friedlander (1971), illustrates the type of information provided by various aerosol instruments in terms of $N_\infty g(t, v, n_1, \dots, n_{k-1})$. The following notation is used to indicate integrations over size, time, and composition:

$$\frac{\int_{t_1}^{t_2} \int_{v_1}^{v_2} \int g dn_1 \dots dn_{k-1} dv dt}{t_2 - t_1} \equiv \overline{\int_{v_1}^{v_2} \int g dn_i dv}. \quad (3)$$

The weighting factor, $W(v)$, for continuous integral measurements depends on the integral aerosol property being measured. Examples of weighting factors

include:

$$\begin{aligned}
 W(v) &= 1.0 && \text{for CNCs,} \\
 W(v) &= \frac{\pi D_p^2}{4} \cdot K_{sp} && \text{for integrating nephelometers,} \\
 W(v) &= \rho_p \cdot v && \text{for mass measurement,}
 \end{aligned} \tag{4}$$

where D_p is the particle diameter, K_{sp} the single-particle scattering efficiency, and ρ_p the particle density. Additional information on integral measurements is available from various sources (e.g., Friedlander, 1977; Hinds, 1982; Seinfeld, 1986).

Because the available instruments use a variety of approaches to measure particle size, different sizes can be reported for the same particle. For example, the “aerodynamic size” obtained with impactors and aerodynamic particle sizers depends on particle shape, density, and size, while the “electrical mobility size” obtained by electrostatic classification depends on particle shape and size but not on density. “Optical sizes”, which are determined from the amount of light scattered by individual particles, depend on particle refractive index, shape, and size. These sizes can be quite different from the “geometric” or “Stokes” sizes that would be observed in a microscope. Converting from one measure of size to another typically involves significant uncertainty. Such conversions, however, are often essential in utilizing aerosol measurements. These observations underline the importance of understanding the means used to measure sizes and of developing techniques to measure such properties including shape, density, and refractive index.

Laboratory calibrations can provide a misleading impression of accuracies that can be achieved when an instrument is used to measure atmospheric aerosols. Similar instruments that have been carefully calibrated in the laboratory may disagree when used for ambient aerosol measurements due to subtle difference in size cuts, or different sensitivities to aerosol hygroscopic properties, particle density or hygroscopicity. Therefore, rather than provide a misleading table of measurement precision and accuracy, I have discussed factors that affect measurement accuracy when discussing individual measurement techniques.

This review of aerosol instrumentation is organized according to the categories suggested by Friedlander with the order of presentation following Fig. 1. We first discuss measurements that provide a single piece of information integrated over size and composition and progress towards instruments that provide more detailed resolution with respect to size and time. We then follow a similar progression for instruments that measure aerosol chemical composition.

Instrument	Measured Quantity and Resolution		
Perfect Single Particle Measurements of Size-Resolved Composition			
	Distribution Function  Size (Continuous)	Measured Quantity = $N_m \cdot g(v)dv$  Time (Continuous)	 Composition (Complete)
Measurements of Integral or Size-Resolved Physical Properties			
"Continuous" measurements of integral properties: CNC CCN mass concentration Epiphaniometer integrating nephelometer photoacoustic spectrometer	Distribution Function  Size	Measured Quantity = $N_m \cdot \int_0^\infty W(v)g(v)dv$  Time: ~Seconds	 Composition
Time-integrated measurements of size-resolved mass: Cascade Impactor	Distribution Function  Size	Measured Quantity = $N_m \cdot \int_{v_1}^{v_2} \rho_p \cdot v \cdot g(v)dv$  Time: Hours	 Composition
Physical size distributions: optical particle counter electrical mobility analyzer aerodynamic particle sizer diffusion battery	Distribution Function  Size	Measured Quantity = $N_m \cdot \int_{v_1}^{v_2} g(v)dv$  Time: ~Minutes	 Composition
Measurements of Integral or Size Resolved Chemical Properties			
Time and size integrated measurements of composition: Filter	Distribution Function  Size	Measured Quantity = $N_m \cdot \int_0^\infty n_j \cdot g(v)dv$  Time: Hours	 Composition
Time-integrated measurements of size-resolved composition: Cascade Impactor Electron Microscopy Laser microprobe	Distribution Function  Size	Measured Quantity = $N_m \cdot \int_{v_1}^{v_2} g(v)dv$  Time: Hours	 Composition
Real-time measurement of individual particle composition Mass spectrometer for individual particle analysis	Distribution Function  Size	Measured Quantity = $N_m \cdot g(v)dv$  Time: ~Seconds	Not Detected  Composition

OPC = Optical Particle Counter
SEMS = Scanning Electrical Mobility Spectrometer
SMPS = Scanning Mobility Particle Spectrometer
CNC = Condensation Nucleus (or Nuclei) Counter
CPC = Condensation Particle Counter (the same as a CNC)

Figure 1. Classification of aerosol instruments according to their capacity to resolve size, time and composition.

A previous comprehensive review on ambient particulate measurements was written by Chow (1995). Chow's paper focuses on fixed-site sampling and includes comprehensive discussions of size-selective inlets, flow measurement, filter media, methods and sensitivities of analytical methodologies, etc. Much of the material that was discussed in Chow's article is pertinent to the NARSTO review, and the reader is referred to her paper for an in-depth critical review of measurements used for compliance monitoring. The present paper complements this earlier review.

2. Aerosol sampling inlets

The ideal aerosol sampling inlet would draw in 100% of the particles in a specified size range and would transport them all without modification to the detector or collector. Unfortunately, obtaining representative samples of aerosols can be difficult. The efficiency with which particles enter the inlet can be more or less than 100% and varies with particle size, wind speed, and direction. Particles can be lost en route from the inlet to the measurement device, and thermodynamic changes in the sampled air can lead to changes in particle size and/or chemical composition. Because problems that are encountered with inlets for fixed-point samplers are distinct from those encountered with aircraft inlets, they are discussed separately.

2.1. Fixed-point sampling

Inlets for fixed-point sampling must operate with minimal maintenance over extended periods in all weather conditions. Size-dependent sampling efficiencies depend on wind speed, and effective samplers deliver nearly 100% of the particles in the size range of interest for the usual range of wind speeds. Most commonly, inlets are designed to deliver all particles smaller than a specified size. Important design characteristics of such inlets include the particle size that is collected with 50% efficiency (i.e., the d_{50}), and the size range over which collection efficiencies rise from 0 to 100% (the "sharpness" of cut). Vincent (1989) presented a systematic discussion of practical and theoretical issues associated with sampler design and evaluation, with a particular emphasis on aspiration efficiencies. Hering (1995) discussed inertial classification techniques that are commonly used to remove particles above a specified "cut" size, and Chow (1995) critically reviewed the literature on size-selective samplers for fixed-point sampling of atmospheric aerosols. In particular, Chow summarized the characteristics of all inlets used in EPA-approved PM_{10} reference or equivalent samplers.

Size-selective inlets typically use inertial classification to remove particles larger than a specified aerodynamic size. The most commonly used inertial classifiers are impactors and cyclones. Conventional impactors accelerate the aerosol through a circular jet or a slit towards an impaction substrate located normal to the axis of the flow. Particles having sufficient inertia cross the flow streamlines to impact on this substrate. An advantage of impactors is that they can easily be designed to provide known size-dependent collection efficiencies (Marple and Liu, 1974,1975; Rader and Marple, 1985) and can be designed with sharper cutpoints than other size classifying devices that use inertial separation. A disadvantage of impactors is that a fraction of the dry, solid particles bounce upon impact (e.g., Dzubay et al., 1976; Wesolowski et al., 1977; Rao and Whitby, 1978; Cheng and Yeh, 1979; Wang and John, 1987a). Bounce can be avoided by coating substrates with oil or grease (Rao and Whitby, 1977; Turner and Hering, 1987; Pak et al., 1992), although such surfaces become ineffective at preventing bounce when heavily loaded (Reischl and John, 1978).

Virtual impactors are also used as size-selective inlets (Loo et al., 1976; Jaklevic et al., 1981a). With a virtual impactor, the impactor collection substrate is replaced by a receiving tube. Particles larger than the aerodynamic cut size are thrown due to their inertia into the receiving tube and delivered by the minor flow (typically 5 to 20% of the total flow) to the coarse particle filter. Particles smaller than the cut size are delivered by the major flow to the fine particle filter. Although laboratory measurements are often required to determine size-dependent losses on the receiving tube, size cuts can be calculated with reasonable confidence (Marple and Chien, 1980). Recent work has extended the flow rates and reduced the size cuts that can be achieved with virtual impactors (Solomon et al., 1983; Marple et al., 1990; Sioutas et al., 1994a-c). Virtual impactors are not affected by particle bounce and reentrainment, and they effectively collect both wet and dry particles without oil or grease-coated substrates, and therefore require less maintenance than conventional impactors when used as size-selective inlets for routine field monitoring.

Cyclones are cone-shaped or cylindrical devices in which the sampled aerosol enters tangentially, rotates several times about the axis, and exits vertically through an opening located on the axis at the top. Particles are transported to the wall by centrifugal force. Liquid particles adhere to the wall, while solid particles settle into a collecting cup located at the bottom of the cyclone. Cyclones are not affected by particle bounce or reentrainment, and they effectively collect both wet and dry particles without oil or grease-coated substrates. Cyclones can be inexpensive and are easy to maintain and operate. Unlike impactors, however, no theory provides reliable design criteria; cyclone performance must be determined empirically (Leith and Mehta, 1973; Chan and

Lippmann, 1977; Dirgo and Leith, 1985; Ramachandran et al., 1991). Also, cyclones tend to be somewhat more bulky than impactors.

Nuclepore filters with large cylindrical pores (5–12 μm) have occasionally been used to provide size-selective inlets (Flocchini et al., 1981; Cahill et al., 1990). Small particles pass through such filters with high efficiency, but large particles do not. John et al. (1983a,b) showed that the size-dependent collection efficiency and the collection mechanism depend on flow rate. At low flow rates interception is the dominant collection mechanism, while inertial collection is dominant at high flow rates. Interception depends on the particles geometric size, while inertial collection depends on aerodynamic size. Evidence for bounce of large, dry particles was observed, leading one to question the effectiveness of these filters as quantitative separators for fine and coarse particles.

2.2. Aircraft sampling

Aircraft used for atmospheric measurements typically fly at speeds ranging from 40 to 200 m s^{-1} while the flow speed through filter samplers or aerosol counting/sizing instrumentation is typically less than 3 m s^{-1} (Jonsson et al., 1995). Furthermore, flight maneuvers lead to variations of $\pm 10^\circ$ in pitch and $\pm 5^\circ$ in roll and yaw (Baumgardner and Huebert, 1993). These sampling conditions lead to significant uncertainty in aircraft aerosol measurements (Baumgardner and Huebert, 1993; Foltescu et al., 1995). Uncertainties arise from the effect of the flow around the airframe on particle size distributions near the probe inlet, unknown efficiencies with which particles of various sizes enter the sampling probe, unknown transport efficiencies through the probe to the particle measurement device, and the increase in the aerosol temperature caused by the rapid deceleration. These uncertainties can lead to measured concentrations that are either greater than or less than the true values.

Work by Huebert and coworkers (Huebert et al., 1990) demonstrated significant particulate species losses for marine sampling with isokinetic aircraft probes (i.e., probes for which the air flow speed through the inlet equals the speed of the aircraft). For an aircraft traveling at 100 m s^{-1} , they found that 50–90% of the sampled sodium deposited within the probe immediately downstream of the inlet where the flow was highly turbulent due to the small probe diameter and the high sampling speed. The fractional loss of sulfate within the probe was less than for sodium but was still significant. Although size distribution data were not available, previous work in a similar environment showed that most sulfate was submicron and most sodium was supermicron. Because losses by turbulent inertial deposition increase with size (Friedlander and Johnstone, 1957; Liu and Agarwal, 1974), they speculated that the higher

losses for sodium likely resulted from its larger mean size. The fact that sulfate losses were significant led them to conclude that losses of submicron particles may have been significant and that "many of the existing literature values for aerosol concentrations above the surface [may possibly be] underestimates of the actual ambient values by factors of 2–10."

Daum and coworkers obtained data which led them to believe that isokinetic probes collect and transport submicron particles with high efficiency, as would be expected based on available theories for aerosol sampling and transport (Belyaev and Levin, 1974; Pui et al., 1987; Rader and Marple, 1988; Tsai and Pui, 1990). They found that concentrations of sulfates measured with an aircraft traveling at 50 m s^{-1} agreed to within experimental uncertainties with concentrations obtained at a fixed site sampler located on the ground (Peter Daum, personal communication, July 1997).

Fahey et al. (1989) took advantage of the non-ideal sampling characteristics of a sub-isokinetic inlet for NASAs ER-2 aircraft to obtain important information on heterogeneous chemical processes in the stratosphere. The air speed into a subsokinetic inlet is less than the speed of the aircraft. Therefore, air streamlines rapidly diverge as they approach the inlet. Particles with sufficient inertia cross streamlines and enter the inlet, leading to an enhancement in the concentration of large particles. They were able to confirm in this way that NO_y is a major constituent of polar stratospheric cloud particles.

Another factor that can play an important role in aerosol sampling is the temperature increase associated with "ram heating", which occurs when the flow speed is rapidly reduced in the probe. These temperature increases are in the range of 5–20°C, depending on the aircraft speed, and lead to evaporation of water and other volatile species. Losses of such species can affect size distributions and chemical composition of the sampled aerosol. Wilson et al. (1992) analyzed the effect of such heating on stratospheric sulfate particles as they traveled through the particle sampling inlet of NASA's ER-2 aircraft, which travels at 200 m s^{-1} , and concluded that sizes decrease by as much as 20%. More problematic than the loss of water, which can be estimated with reasonable confidence, is the loss of other labile species such as nitric acid, that are present in unknown quantities. Difficulties in measuring such species have made it difficult to quantify the composition of polar stratospheric cloud particles (Marti and Mauersberger, 1993; Molina et al., 1993; Worsnop et al., 1993).

Experts who participated in the 1991 Airborne Aerosol Inlet Workshop in Boulder, CO (Baumgardner and Huebert, 1993) concluded that more work on aircraft particle sampling inlets is required. They recommended a three-part program that includes modeling, aircraft studies, and wind tunnel studies. There has since been significant progress on this topic. Seebaugh and Lafleur (1996) have shown that it is possible to draw a portion of the flow through

porous walls of conical inlets, thereby drastically reducing the development of turbulent flow within the probe. Theory suggests that particle deposition should be negligible if turbulence is negligible. Other investigators have used multiple diffusers to reduce flow speeds and shrouded inlets to both reduce speeds and align particles with the sampling inlet so as to permit isokinetic sampling.

3. Measurements of aerosol physical properties

3.1. *Integral measurements*

Instruments that provide totals (integrals) of specified variables over a given size range are often used for aerosol measurement. For example, condensation nucleus counters provide the total number concentration of particles larger than a minimum size, and cloud condensation nuclei counters measure the subset of particles that can form cloud droplets when exposed to water vapor at a specified supersaturation. Filter samplers are often used to measure total mass concentrations, integrated with respect to both size and time. The introduction and Fig. 1 provide graphical and mathematical explanations of integral versus size-resolved aerosol measurements.

3.1.1. *Number concentration*

Condensation nucleus counters (also referred to as condensation particle counters or Aitken Nuclei Counters: CNCs, CPCs, ANCs) measure the total aerosol number concentration larger than some minimum detectable size. In addition to their use in studies of aerosol climatology, CNCs are often used as detectors with other instruments such as electrical mobility classifiers (Keady et al., 1983). Recent health effects studies have suggested that particulate health effects may be more sensitive to number concentration than to mass (Oberdörster et al., 1995).

Particles are grown by condensation in CNCs until they are sufficiently large to be detected optically. Diameter growth factors as large as 100–1000 are common, so the original particle constitutes only a minuscule fraction ($\sim 10^{-3}$ – 10^{-9}) of the detected droplet. CNCs can detect individual particles as small as $0.003\ \mu\text{m}$ ($\sim 10^{-20}$ g), so they provide an extraordinarily sensitive means for detecting small amounts of material. A variety of substances have been used as the condensing vapor, but water and *n*-butyl alcohol are currently used most often. Because the supersaturation of the condensing vapor is very high, the response of CNCs is typically insensitive to the composition of the measured particles.

CNCs are often categorized according to the method used to produce the supersaturated vapor. Expansion-type CNCs were predominant until the introduction of steady-flow, forced-convection heat transfer instruments (Sinclair and Hoopes, 1975a,b; Bricard et al., 1976). In the latter instruments, supersaturation is achieved when the saturated aerosol at $\sim 35\text{--}40^\circ\text{C}$ enters a laminar-flow cylindrical condenser. Supersaturation is achieved by heat transfer from the warm aerosol to the walls of the condenser, which are typically maintained at $\sim 10^\circ\text{C}$. It is advantageous to use a high molecular weight working fluid with instruments of this type to ensure that sufficient cooling (and therefore supersaturation of the vapor) occurs before the vapor is depleted by condensation on the cool walls. The working fluid should also have a vapor pressure that is high enough to cause particles to grow to $\sim 10\text{ }\mu\text{m}$ during the $\sim 0.3\text{ s}$ flow time through the condenser but low enough to ensure that the vapor is a small fraction of the total gas flow. *n*-butyl alcohol is commonly used because it meets these requirements. Steady-flow, forced-convection instruments are the most commonly used CNCs today due to their reliability and accuracy. Steady-flow instruments that achieve supersaturation by mixing cool and warm saturated air streams have also been reported and commercialized (Kousaka et al., 1982, 1992), although they have seen only limited application for atmospheric measurement.

CNCs can also be categorized as direct or indirect detection instruments. Direct (or single-particle-counting) instruments determine particle concentrations by counting individual droplets formed by condensation. The original expansion-type instruments of John Aitken (Aitken, 1890, 1891) involved the use of a microscope to manually count individual droplets collected from a known volume of air onto a grid, and today's commercially available steady-flow instruments use automated single-particle counting if concentrations are low enough ($<10^3\text{--}10^4\text{ cm}^{-3}$, depending on the instrument design). Indirect measurement of particle concentration is achieved by measuring light attenuation through or the light scattered by the "cloud" formed by vapor condensation. Such indirect measurements require calibration with an independent concentration standard. The design of indirect-detection expansion-type CNCs culminated with the manually operated Pollak Model 1957 (Metnieks and Pollak, 1959). This instrument uses a photoelectric detector to measure the transmittance of light along the axis of a cylindrical expansion chamber. Concentrations are inferred from the measured attenuation based on a calibration scheme that involved dilution to levels that were low enough to permit measurement by manual counting techniques (Nolan and Pollak, 1946). The accuracy of measurements with the Model 1957 has been confirmed by an independent calibration (Liu et al., 1975), and the Model 1957 is still in limited use today.

The accuracy of concentrations determined by CNCs depends on the detection scheme. Uncertainties for single-particle-counting instruments are determined primarily by uncertainties in aerosol sampling rate, Poisson counting statistics, and the minimum detectable size. Uncertainties in measurements with indirect counting instruments depend on calibration accuracy, instrument stability, signal-to-noise, minimum detectable size, and sampling line losses. Under most practical situations for atmospheric sampling, accuracies of $\sim 10\%$ are typical, although discrepancies can be much greater if high concentrations of nanoparticles (particles smaller than ~ 20 nm) are present. This is because the fraction of nanoparticles that is detected varies with instrument design, and because the counting efficiency of nanoparticles can also be affected by vapor depletion due to preferential condensation on "large" particles in the condenser. For example, in comparisons of CNCs operating on NCAR's C-130 aircraft during ACE-1, Weber et al. (1999) found that when nucleation was not occurring a TSI 3760, a TSI 3025 and a University of Minnesota prototype ultrafine CNC agreed, on average, within 4%. Two other instruments were, on average, 20 and 65% lower than these. Post-campaign measurement revealed that these latter measurements were affected by flow calibration errors. When nucleation was occurring (i.e., when concentrations of particles in the 3–4 nm range were high), the average concentrations of the TSI 3760, the TSI 3025 and the University of Minnesota prototype instrument were, respectively, 1045, 1577, and 2854 cm^{-3} , illustrating the sensitivity of the lower detection limit to measured total number concentrations. Measurements of CN concentrations on the R/V Discoverer, a NOAA ship, were about 20% below values measured on the C-130 nearby, while measurements at Cape Grim, a ground station, were within 4% of C-130 values.

The minimum detectable size and the size-dependent detection efficiencies of CNCs vary significantly with the instrument design and sampling pressure (Liu and Kim, 1977; Wilson et al., 1983a, b; Bartz et al., 1985; Wiedensohler et al., 1997). The key variables that affect the minimum detectable size are transport efficiency to the condenser and the vapor supersaturations to which particles are exposed. Due to the effects of curvature on vapor pressure (Thompson, 1871), the supersaturation that is required to activate particles increases with decreasing size. Particles of ~ 3 nm require supersaturations of several hundred percent; 3 nm is near the lower detection limit of CNCs because new particles are produced by self-nucleation of the vapor when supersaturations ratios are increased beyond this. Stolzenburg and McMurry (1991) designed an instrument that provides high detection efficiencies for particles down to 3 nm. Pressure affects the performance of steady-flow CNCs through its effect on heat and mass transfer (Bricard et al., 1976; Wilson et al., 1983a, b; Zhang and Liu, 1991; Saros et al., 1996). Instruments that function at pressures down to 40 mbar (21.5 km altitude) have been developed.

3.1.2. Cloud condensation nuclei concentrations

Cloud condensation nuclei (CCN) counters measure the concentration of particles that are converted to cloud droplets by condensation of water (i.e., “activated”) at a specified supersaturation. CCN concentrations depend on both the aerosol size distribution and the aerosol composition (Junge and McLaren, 1971; Fitzgerald, 1973; Pruppacher and Klett, 1980; Harrison, 1985). Particles down to $\sim 0.04 \mu\text{m}$ diameter can serve as cloud condensation nuclei. CCN measurements are of central importance in determining the influence of anthropogenic particles on the atmosphere. For example, a significant fraction of the sulfate aerosol production in the atmosphere occurs in cloud droplets (Schwartz, 1989), and particulate pollution may increase cloud albedo, thereby decreasing the Earth’s net incoming radiative energy (Twomey et al., 1984; Twomey, 1991). 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.

Unlike CNCs, 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 (~ 0.01 to $\sim 1\%$). Therefore, the CCN concentration is a fraction of the CNC concentration and depends on the supersaturation employed. The saturation ratio that is required to activate particles increases with decreasing size. Important design parameters for CCN counters include the range of saturation ratios for which information can be obtained, the method used for determining the relationship between CCN concentrations and saturation ratio, and the particle growth time (for example, 100 s is required to achieve equilibrium for supersaturations of 0.01% (Hoppel et al., 1979)). Most CCN instruments use thermal gradient diffusion chambers to produce the desired supersaturations.

The Third International CCN Intercomparison Workshop was held in Reno, NV, in 1980 and involved nearly all CCN instruments in the world at that time including 9 static thermal gradient diffusion cloud chambers (STGDCC), 5 continuous flow diffusion cloud chambers (CFDCC), 4 isothermal haze chambers (IHC), and 2 diffusion tubes. The reader is referred to the special issues of *Journal de Recherches Atmosphériques* (1981, pp. 181–373) for a complete discussion of the results of this most recent workshop. A more recent review of CCN instruments is provided by Hudson (1993). The following discussion summarizes observations from these reviews.

Isothermal haze chambers (IHCs) (Fitzgerald et al., 1981) are used to measure concentrations of CCN that are activated in the low supersaturation (0.015–0.15%) range. The principle of operation of these instruments was first described by (Laktionov, 1972), who showed that there exists a unique rela-

tionship between the critical supersaturation required to activate a particle and its equilibrium size at 100% relative humidity. In IHCs, therefore, size distributions of aerosols are measured after they are exposed for an extended period of time to an atmosphere at 100% relative humidity. Optical particle counters are typically used to measure size distributions. Accurate results require accurate measurements of both droplet size and concentration. Such measurements are subject to sizing errors associated with droplet evaporation in the warm optical particle counter and differences between the refractive index of the water droplets and that of the calibration aerosols. An advantage of this technique is that a single measurement provides the spectrum of droplets that are activated over the specified range. The useful range of supersaturations for this technique is limited by the minimum size that can be detected optically. Two of the four IHCs tested during the Third International Workshop agreed to within 40% over the entire supersaturation range tested, while discrepancies for the other instruments exceeded this.

Diffusion tubes (Leaitch and Megaw, 1982) function in the 0.04–0.3% supersaturation range. These instruments involve steady flow through a heated, wetted tube. Because water vapor diffuses faster than heat, the aerosol along the centerline of the tube becomes supersaturated. The radial and axial saturation ratio profiles within the tube depend on the inlet relative humidity and on the temperature difference between the tube walls and the incoming aerosol. In practice, theory is used to calculate the saturation ratio profiles based on operating conditions. An optical particle counter is used to measure droplet distributions downstream of the diffusion tube. Theory for activation and growth of particles of known composition is then applied to these data to infer the CCN concentration at an effective average supersaturation corresponding to operating conditions. Limitations of this technique are that particle composition must be known, and an extended time (~ 45 min) is required to scan through a range of supersaturations. Also, the OPC measurements have limitations similar to those encountered with IHCs.

Static thermal gradient diffusion cloud chambers were the first commonly used type of CCN counter (Twomey, 1967). The vast majority of instruments used in the first two international workshops were of this type. These instruments consist of two wetted surfaces maintained at different temperatures. Water vapor is saturated at each of the surfaces but rises to a peak supersaturation at a point between the surfaces due to the nonlinear dependence of vapor pressure on temperature. Photographic or optical techniques are used to count droplet concentrations at the location of this peak supersaturation (Juisto et al., 1981). By operating over a range of temperature differentials, the relationship between CCN and supersaturation is determined. In practice, measurements are limited to the 0.1 to 1.0% supersaturation range. A limitation of this approach is that a long time is required to carry out measurements over

a range of supersaturations due to the time required for thermal stabilization. Nine different static thermal gradient instruments were compared during the Third International Workshop. It was found that five of these typically agreed to within 20%; 10% agreement was achieved at 1% supersaturation. Discrepancies among the remaining instruments were greater than this, due in part to the newness and/or lack of previous calibration for these instruments.

Continuous flow diffusion cloud chambers (CFDCCs) involve flow between wetted parallel plates that are maintained at different temperatures (Hudson and Alofs, 1981). As with static diffusion chambers, the water vapor supersaturations achieve a peak value at some point between the plates. An optical counter measures the droplet concentration at the exit from the chamber along the streamline that is exposed to the peak supersaturation. Measurements are made at several temperature differentials to determine the relationship between CCN concentration and supersaturation. Again, a significant time is required to complete a single measurement. The five instruments tested during the Third International Workshop typically agreed to within 15%.

Several CCN spectrometers have been developed that permit rapid measurements of CCN-supersaturation spectra. The instrument of Radke et al. (1981) involves four continuous flow diffusion cloud chambers operated in parallel, each with a different temperature difference, thereby providing near-real-time measurements of CCN concentrations at four saturation ratios in the 0.1–1% range. This instrument was designed for aircraft use where rapid measurements are necessary. The University of North Carolina spectrometer (Fukuta and Saxena, 1979) involves flow through a rectangular channel, as in CFDCCs. In contrast to CFDCCs, however, the temperature gradient is maintained across the width of the channel rather than between the two larger plates. Thus, the supersaturation varies across the channel. An optical particle counter is moved across the width of the channel to obtain the CCN-supersaturation relationship. Measurements require about 30 s, and operation is limited to supersaturations above about 0.1%. Hudson's "instantaneous" CCN spectrometer (Hudson, 1989) provides information on the CCN-supersaturation spectrum over the 0.01 to 1% range at a rate of ~ 1 Hz. This instrument is similar in design to a CFDCC but is different in that CCN spectra are obtained from droplet size distributions measured with an optical particle counter at the exit of the instrument, much as is done with the IHC. The relationship between the final droplet size and the initial size is obtained by calibration with monodisperse particles of known composition. This instrument has seen a great deal of use on aircraft due to its fast time response and broad supersaturation range.

The CCN apparatus of Khlystov et al. (1996) is unique for its ability to handle large volumetric flows ($30 \text{ m}^3 \text{ min}^{-1}$), thereby it can be equipped with instrumentation designed for in-cloud studies. While not designed for routine measurements of CCN concentrations, this apparatus will provide new infor-

mation on the influence of anthropogenic aerosols on the formation and microstructure of marine clouds.

CCN counters in use today are mostly laboratory prototype instruments rather than standard commercial products. Intercomparison workshops have led to higher confidence in the accuracy of particular instruments, but measurements made by different groups are not necessarily comparable. Furthermore, because the tendency of the atmosphere to produce clouds depends upon supersaturation, it is essential to carry out CCN measurements with instruments that operate in a relevant supersaturation range. Establishing the relationship between the size-resolved composition of ambient aerosols and their cloud nucleating characteristics is essential for developing valid models for the “indirect” effect of aerosols on radiative forcing and in-cloud chemical transformations.

3.1.3. Particle mass concentrations

Measurements of particulate mass concentrations are important for regulatory and scientific reasons. The current US National Ambient Air Quality Standard for particulate matter applies to mass concentrations smaller than 10 μm aerodynamic diameter, and a new standard for mass concentrations of particles smaller than 2.5 μm aerodynamic diameter has been promulgated (Federal Register, 1997). Federal Reference Methods for these mass measurement techniques are discussed later in the paper. While research studies tend to focus on speciation and size, it is essential to be able to reconcile measured mass concentrations with the sum of measured species. Therefore, mass concentrations are also routinely measured in aerosol research studies. In this section the various techniques that are used to measure mass concentration are discussed.

3.1.3.1. Manual methods. The most commonly used technique for measuring particulate mass concentrations involves filtration. 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.

Fiber, membrane, granular bed and Nuclepore filters made from a wide variety of materials are used to collect aerosols (Lippmann, 1989; Lee and Ramamurthi, 1993; Chow, 1995). The physics of particle collection by filters is similar for all types of filters. Particles smaller than about 0.1 μm are collected by diffusion. Because particle diffusivities increase with decreasing size, collection efficiencies increase as size drops below $\sim 0.1 \mu\text{m}$. Particles larger than about 0.5 μm are collected by interception and impaction. Collection efficiencies by these mechanisms increase with increasing size. Therefore, collection

efficiencies tend to increase with increasing size above 0.5 μm . It follows that the “most penetrating particle size” typically falls between 0.1 and 0.5 μm . The value of this most penetrating particle size depends on the filter characteristics and the flow rate through the filter (Lee and Liu, 1980). Many filters that are used for aerosol measurement collect all particles with >99% efficiency. The collection efficiency of loosely woven fiber filters or membrane filters having large pore sizes tend to be less than this, however (Liu et al., 1983).

Analytical sensitivities for gravimetric analyses are currently about $\pm 1 \mu\text{g}$. Therefore, the analytical uncertainty for a 24-h sample obtained using the proposed EPA $\text{PM}_{2.5}$ reference method sampler, which operates at $1.0 \text{ m}^3 \text{ h}^{-1}$, would ideally be $0.04 \mu\text{g m}^{-3}$. Measurements have shown that actual uncertainties are substantially greater than this. Factors including water adsorption/desorption by the filter media, adsorption or volatilization of reactive species, particle losses associated with handling, etc., lead to these higher uncertainties in gravimetric measurements. The Federal Reference Method for $\text{PM}_{2.5}$ indicates that the lower detection limit for mass concentration is $\sim 2 \mu\text{g m}^{-3}$.

Side-by-side measurements with identical samplers and replicate measurements on a given sample permit one to establish the precision with which filter samplers can measure mass concentrations. Determining measurement accuracy is more problematic. Filter measurements are affected by vapor adsorption on substrates (McMurry and Zhang, 1989; Hering et al., 1990; McDow and Huntzicker, 1990), by evaporative losses of semivolatile compounds during or after sampling (Smith et al., 1978; Appel and Tokiwa, 1981; Dunwoody, 1986; Wang and John, 1988; Witz et al., 1990; Eatough et al., 1993), and by reactions between collected particles and substrates (Smith et al., 1978). The extent of these processes varies with location depending on the aerosol mass concentration and composition and temperature and relative humidity. It is likely that such measurement errors are substantially in excess of reported measurement precision.

For more complete information on filter gravimetric measurements, the reader is referred to the review paper of Chow (1995), in which she provided a comprehensive discussion of the relative merits and disadvantages of currently available size-selective inlets, filter sampling media, and filter holders for gravimetric analyses.

3.1.3.2. Automated methods. Automated methods for measurements of aerosol mass concentrations are discussed by Williams et al. (1993). Available methods include the beta gauge, piezoelectric crystals, and the oscillating element instruments. These techniques are briefly reviewed below.

Beta gauges. Beta gauges measure the attenuation of 0.01–0.1 MeV beta particles from a radioactive source through a particle-laden filter. Attenuation

results from scattering of the beta particles by atomic electrons in the filter media and by the deposited particles and is therefore determined by the areal density of atomic electrons. Except for hydrogen, which usually constitutes a small fraction of the particulate mass, the ratio of atomic number to mass is nearly independent of element, and ranges from 0.38 to 0.50. For the elements that constitute the majority of the atmospheric particulate mass (C, Ca, Cl, Fe, Mg, N, O, K, Si, Na, S), however, this ratio ranges from 0.47 to 0.50. For ammonium sulfate, which contains a significant amount of H, the ratio increases to 0.53. Thus, errors associated with the assumed ratio of atomic number to mass may be roughly 10%. In practice, Beta gauges are calibrated with ambient aerosols to minimize this error.

Particle mass loadings are determined from the increase in attenuation that is measured as particles are added to the filter. Experimental studies of Beta gauges show that measurement precision tends to be poorer for instruments used for routine ambient monitoring than for instruments used under controlled laboratory conditions. Early studies with beta gauges show that precisions on the order of $25 \mu\text{g cm}^{-2}$ can be achieved with monitoring instruments (Husar, 1974), while $\sim 5 \mu\text{g cm}^{-2}$ is possible in careful laboratory experiments (Jaklevic et al., 1981b; Courtney et al., 1982). Courtney et al. concluded that mass measurements by beta attenuation are in good agreement with gravimetric mass measurements, and that the advantages of automation make beta attenuation an attractive alternative. Macias and Husar (1976) argued strongly for the utility of mass measurements by beta attenuation. Two commercially produced beta gauges have been designated by EPA as Equivalent Methods for measuring sub- $10 \mu\text{m}$ particulate mass concentrations (PM-10).

Piezoelectric crystals. Piezoelectric crystals undergo mechanical deformations when an electrical potential is applied across certain crystal planes (Ward and Buttry, 1990). If a periodic potential is applied, then the crystal will expand and contract periodically. Crystals have a resonant vibrational frequency that depends on the crystalline material and thickness. This resonant frequency can be altered by adding mass to a vibrating surface. Piezoelectric crystal mass monitors determine aerosol mass loadings by measuring the change in this resonant frequency caused by the deposition of particles from a known volume of air. The use of piezoelectric crystals for monitoring ambient particulate mass loadings has been reviewed by Lundgren et al. (1976) and Williams et al. (1993).

Piezoelectric crystals used for particulate mass monitoring typically consist of quartz cut on the AT crystallographic planes and have natural resonant frequencies, of 5–10 MHz. The sensitivity of this resonant vibrational frequency to incremental mass are typically $10^3 \text{ Hz } \mu\text{g}^{-1}$, and stabilities of $\pm 0.5 \text{ Hz}$ at 10 MHz can be achieved. The change in the frequency of the particle-laden crystal is determined by electronically mixing its resonant frequency with that

from an identical crystal maintained at the same thermodynamic conditions. The difference, or beat, signal is proportional to the particulate mass loading.

Piezoelectric crystals can measure particulate masses as small as 1 ng, although loadings of tens of ng are typically used for measurement. Nonlinearities in the relationship between Δf and Δm typically become significant when mass loadings exceed 5 to 10 μg , at which point the deposition surface must be cleaned. The need to provide such routine maintenance is a disadvantage for instruments that are used for routine monitoring purposes. Other sources of error that have been reported include sensitivity to temperature and relative humidity and poor mechanical coupling between some particle types and the oscillating surfaces, which invalidates the relationship between frequency change and mass increment.

Several instruments that utilize piezoelectric crystals for measuring particulate mass concentrations in the 10 $\mu\text{g m}^{-3}$ to 10 mg m^{-3} range are available. None of these instruments are designated by EPA as an Equivalent Method for measurements of particulate mass concentration.

Work with surface acoustic wave (SAW) mode microbalances has also been reported (Bowers and Chuan, 1989). This approach involves the creation of surface waves by a pair of electrodes on a common surface. Resonant frequencies produced in this way can be much higher than are achieved with AT-cut crystals, leading to much higher mass sensitivities. Sampling using SAW mode microbalances has been reported for situations where aerosol loadings are extremely low, such as in rockets used to sample stratospheric aerosols.

Harmonic oscillating elements. The unique component of the harmonic oscillating element instruments (Patashnick and Rupprecht, 1991) is a tapered tube, the wide end of which is mounted to a rigid base. Particles are collected on a replaceable 0.5 cm diameter filter that is mounted on the narrow end of the tapered element, which is free to oscillate. The element vibrates at a frequency that depends on its geometrical and mechanical properties and on the mass of the filter. As particles are collected on the filter, the element's natural frequency of oscillation decreases. An optical system is used to measure the natural oscillation frequency; oscillations are induced electrically.

The resonant frequency of the tapered element is affected by thermal expansion and contraction associated with temperature fluctuations. Therefore, these instruments must operate at constant temperature. For ease of operation, this temperature is fixed at a value in excess of ambient values, typically 50°C, which exacerbates the loss of semivolatile compounds. Lower temperatures (30°C) were tried in the San Joaquin Valley during the winter of 1995, however, condensation and evaporation of water vapor on the filter during high humidity events negated the measurements (Solomon 1997, personal communication, PG & E, San Ramon, CA).

Harmonic oscillating element instruments provide a very sensitive technique for particulate mass measurements. The mass resolution for 10-min samples is $\pm 5 \mu\text{g m}^{-3}$. Based on comparisons with EPA's designated reference method when sampling ambient aerosols, a commercially available instrument of this design was designated an equivalent method for PM-10 monitoring.

3.1.4. *Epiphaniometer*

The epiphaniometer (Gäggeler et al., 1989) measures the diffusion-limited mass transfer rate of a gas to aerosol particles. These measurements provide information on the maximum possible rates of vapor condensation to or gas reaction with the aerosol. The epiphaniometer also provides a sensitive, real-time measurement of an integral aerosol property (Baltensperger et al., 1991).

Measurements involve adding the gas-phase radioactive isotope ^{211}Pb to the aerosol. The ^{211}Pb , which is produced from a ^{227}Ac source, diffuses and attaches to the aerosol particles. After exposure to the ^{211}Pb for about 2 min, particles are collected on a filter where the amount of attached ^{211}Pb is measured using an α detector.

The mass transport rate of gases to particles occurs at a rate that is proportional to particle surface area (particle diameter squared) for particles that are small compared to the mean free path of the gas ($\sim 0.067 \mu\text{m}$ for air at normal temperature and pressure). Mass transport rates vary in proportion to particle diameter for particles that are large compared to the mean free path. Atmospheric aerosols fall mostly in the "transition" regime, where neither of these simple limiting cases applies. The integral aerosol property that is proportional to the gas mass transfer rate is often referred to as the "Fuchs surface," and the Epiphaniometer directly measures the value of this integral. Theoretical expressions that enable one to calculate the "Fuchs surface" from the aerosol size distribution are given by Fuchs and Sutugin (1970) and by Davis and Ray (1978) among others.

3.1.5. *Aerosol optical properties*

The appearance of a distant object viewed through the atmosphere is affected by several factors: the amount and color of light emitted by the object (initial radiance); the transmittance of that light from the object to the observer; and the scattering of ambient light into the sight path by the atmosphere (path radiance) (Duntley et al., 1957; Malm, 1979; Richards, 1988). Transmittance is determined by the scattering and absorption of light as it traverses the atmosphere. Because the initial radiance, transmittance, and path radiance are sensitive to the wavelength of the light, one must know how those factors depend on wavelength before optical effects such as visibility impairment or

atmospheric albedo can be characterized fully. Middleton (1952) provides a comprehensive discussion of atmospheric visibility and its measurement, and Quinn et al. (1996) and McMurry et al. (1996a,b) discuss the measurement of aerosol optical properties. We focus here on point measurements of aerosol scattering and absorption coefficients.

A significant issue in the measurement of atmospheric optical properties is the replacement of human observers by the Automated Surface Observing System (ASOS) at airports which is currently underway. Although data from human observers are qualitative, they provide a comprehensive historical record that has been useful for assessing visibility trends across the US ASOS instrumentation measures the amount of light scattered in the forward direction with a time resolution of 1 min. Because ASOS is used for flight safety, it does not record data for visibilities exceeding 10 miles. However, a recent study by Richards et al. (1997) showed that ASOS equipment is capable of measuring scattering at aerosol concentrations as low as $\sim 10 \mu\text{g m}^{-3}$. It would be sensible to record ASOS data routinely at the highest time resolution and sensitivity possible. This could be done at a nominal cost, and would serve to ensure a long-term record at a consistent set of measurement sites.

3.1.5.1. Scattering coefficient. Integrating nephelometers (Beuttell and Brewer, 1949) measure the total amount of light scattered by an aerosol. The “integration” covers scattering angles from near forward to near backward. To determine the contribution of gases and electronic noise to the scattering signal, the instrument’s light scattering response to filtered air is measured periodically. The contribution of particles to scattering is then determined by difference. When equipped with a photon-counting detector (Charlson et al., 1974), the integrating nephelometer can measure particle light scattering coefficients of less than 0.1 Mm^{-1} , a value equal to about 1% of the light scattering coefficient of particle-free air at normal atmospheric pressure. The design and applications of the integrating nephelometer were recently reviewed by Heintzenberg and Charlson (1996).

Because of its potential for high accuracy, portability, and moderate cost, the nephelometer has been used widely for measurements of light scattering coefficients. There are, however, several sources of measurement error with this instrument. First, the contributions of coarse particles (particle diameter greater than about $5 \mu\text{m}$) to scattering are underestimated because they tend to deposit at the inlet. Such inlet losses increase strongly with size. Second, the optics do not permit measurement of light scattered in the near forward direction (between 0° and $5\text{--}10^\circ$, depending on the instrument design). The magnitude of this truncation error is typically $\sim 10\text{--}15\%$ for submicron particles (Ensor and Waggoner, 1970; Sloane et al., 1991; Anderson et al., 1996a). However, because large particles scatter strongly in the forward direction, truncation errors

can be as large as 50% for particles of $\sim 5 \mu\text{m}$. Finally, errors caused by droplet evaporation due to heating of the aerosol can be significant, especially at high relative humidities ($>90\%$), where water constitutes most of the particle volume.

Two new nephelometers have recently become commercially available. The Optec NGN-2 (Malm et al., 1996) is an "open air" design which minimizes errors associated with inlet losses and with heating. Scattering is measured between 5 and 175° for illuminating radiation centered at 550 nm . The TSI 3563 measures total scattering ($7\text{--}170^\circ$) and back scattering ($90\text{--}170^\circ$) for monochromatic radiation at 450 , 550 , and 700 nm . Back scattering is of particular importance in evaluating the contribution of aerosols to the Earth's albedo in climate-effects studies. Intercomparisons of field measurements during the Southeastern Aerosol and Visibility Study (SEAVS) in the summer of 1995 showed that three Optec NGN-2 instruments agreed with each other to within 3%. Green light scattering (550 nm) measured with the TSI 3563 was, on average, 70% of the value measured by the Optec instruments at relative humidities less than 60%. These instruments were found to agree to within about 3% after data were corrected to account for differences in illuminating radiation and instrument truncation angles (Saxena et al., 1996). At higher relative humidities, agreement tends to deteriorate because small differences in relative humidities at the point of measurement can lead to significant differences in scattering. These results show that accurate assessments of sunlight scattering by atmospheric aerosols require that instrumental measurements be corrected for truncation, for differences in illuminating radiation, and for subtle differences between the relative humidity at the point of measurement and in the atmosphere.

Although the amount of light that an aerosol with a given mass concentration scatters depends on its size distribution, measurements have shown that the ratio of the dry scattering coefficient to the dry fine particle mass concentration measured at various locations does not vary a great deal. For example, Charlson et al. (1968) found that this ratio (referred to as the dry fine particle mass scattering efficiency) measured at New York, San Jose, and Seattle averaged $3.3 \text{ m}^2 \text{ g}^{-1}$, with a range of 1.5 to $5.6 \text{ m}^2 \text{ g}^{-1}$.

Information on wavelength-dependent light scattering provided by multi-wave length nephelometers provides useful information on aerosol size distributions (Thielke et al., 1972; van de Hulst, 1981). It is often found that within the optical subrange ($\sim 0.16\text{--}1.2 \mu\text{m}$; Junge, 1963) the light scattering coefficient, b_{sp} , and aerosol size distribution function, dN/dD_p , obey the following power-law relationships:

$$b_{\text{sp}} = C\lambda^{-\alpha}, \quad (5)$$

where α is referred to as the Angstrom exponent, and

$$\frac{dN}{dD_p} = K \cdot D_p^{-\nu}. \quad (6)$$

Power-law aerosol size distribution functions of this form are referred to as Junge distributions. When these relationships apply it can be shown that

$$\alpha = \nu - 3. \quad (7)$$

Thus, if b_{sp} depends strongly on wavelength (large α), then the size distribution function decreases strongly with size. Measurements have shown that values of α tend to be higher for continental aerosols than for clean marine aerosols (Ogren, 1995).

3.1.5.2. Absorption coefficient. Absorption coefficients are most commonly inferred from measurements on particles collected on filters. However, the viability of conducting in-situ measurements using photoacoustic spectrometry has also been demonstrated. These techniques are discussed in this section.

Filter techniques are the most common methods for measuring particle absorption coefficients. Because light transmittance through filters is affected by scattering and absorption, the effects of scattering, including multiple scattering, must be accounted for. If light interacts with more than one particle as it passes through the filter, the apparent absorption coefficient will exceed the correct value. Also, filter techniques are problematic because the optical properties of deposited particles may be different from those of airborne particles, especially if the particles undergo chemical reactions on the filter.

Lin et al. (1973) developed the integrating plate technique for measuring absorption coefficients of particle deposits on filters. With this method, an opal glass plate is located between the filter and the optical detector. Because the opal glass is a diffuse reflector, light scattered by particles in the forward direction is detected with the same efficiency as light that enters the glass directly. If backward scattering is small in comparison to absorption, changes in filter transmittance before and after particle collection can be attributed to particle absorption. Lin et al. concluded that neither backward scattering nor multiple scattering contributed significantly to errors in their measurements. This technique was modified somewhat by Clarke (1982) to improve measurement accuracy. Clarke reports that with his modifications this technique can measure absorption coefficients as low as 0.005 Mm^{-1} for a 10-h sampling period.

Hänel (1987) argued that multiple scattering and backward scattering led to significant errors in absorption coefficients measured by previous investigators using filter techniques. He developed an approach for measuring absorption coefficient that permitted accounting for forward, backward, and multiple

scattering from collected particles. Reported values for absorption coefficients using this approach are somewhat smaller than values determined with other techniques.

The earliest and simplest method of measuring light absorption by particles on filters is the coefficient of haze (COH) technique (Hemeon et al., 1953). The aethalometer described by Hansen et al. (1984) involves an updated and more sensitive absorption measurement that operates on a similar principle. These techniques measure the light attenuation caused by an aerosol sample on a filter; no integrating plate is used to correct for light scattering. Wolff et al. (1983) found a good correlation between COH and concentrations of elemental carbon, and Campbell et al. (1989) found good correlations between COH and absorption measurements using an integrating plate and integrating sphere. Commercially available aethalometers provide continuous, near real-time data and have been used for monitoring. Quantification is achieved by calibrating against a more accurate absorption measurement standard.

Photoacoustic spectroscopy measures the absorption coefficients of suspended particles in real time (Adams, 1988). Work on a small and very sensitive photoacoustic instrument that shows promise for field measurements was recently reported by Moosmüller and coworkers (Arnott et al., 1995, 1999; Moosmüller et al., 1997a,b). In these instruments, the air stream, from which NO_2 has been removed, is drawn into an acoustic cell where it is illuminated by light that is modulated at the resonant frequency of the cell. Light energy absorbed by the particles heats the carrier gas, which expands and then contracts according to the modulation frequency of the light. The associated pressure variation is a sound wave whose intensity can be measured with a microphone. Adams (1989) reports a sensitivity of 3 Mm^{-1} for absorption coefficients measured with her instrument, while Moosmüller reports a sensitivity of $0.4\text{--}0.5 \text{ Mm}^{-1}$ for his. Because photoacoustic spectroscopy involves measurements on gas borne particles and is therefore not affected by errors inherent to filter-based techniques, it is conceptually the best available technique for measuring particle absorption coefficients. However, it requires skilled personnel and complex equipment that is not commercially available. Therefore, it is not yet suitable for routine monitoring.

Aerosol absorption coefficients are frequently inferred from measurements of "elemental carbon" concentrations. Obtaining an accurate value for absorption coefficients with this approach requires (1) an accurate measurement of the elemental carbon concentration, (2) knowledge that elemental carbon is the only significantly absorbing particulate species, and (3) knowledge of the elemental carbon "mass absorption efficiency". Foot and Kilsby (1989) compared particle absorption coefficients measured with a filter technique with those measured with a photoacoustic technique. They used laboratory particles with known properties and found that agreement between the two meth-

ods was $\pm 15\%$. Measurements in Los Angeles during the Southern California Air Quality Study (SCAQS) showed that absorption coefficients measured with a photoacoustic spectrometer agreed, on average, to within about 10% ($r = 0.926$) of values obtained from elemental carbon concentrations measured with a thermal-optical technique (Turpin et al., 1990a) assuming a mass absorption efficiency for elemental carbon of $10 \text{ m}^2 \text{ g}^{-1}$. In a previous study designed to compare nine techniques for measuring elemental and organic carbon concentrations it was found that the ratio of the method mean to the grand mean for all elemental carbon measurements for these nine techniques ranged from 0.43 to 1.48 (Hering et al., 1990). Therefore, different techniques for measuring elemental carbon concentrations will lead to estimates of absorption coefficients that vary by a factor of ~ 3 for a given value of the mass absorption efficiency.

3.2. Size-resolved measurements

3.2.1. Optical particle counters

Single-particle optical counters (OPCs) 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 proportional voltage pulse. Particle size is determined from the magnitude of this voltage pulse by using a calibration curve typically obtained from measurements using spherical particles of known size and composition. Pulse height and area are commonly used measures of pulse magnitude. Size distributions are obtained by measuring the distribution of pulse magnitudes obtained from a representative population of particles. A review of aerosol measurement by light scattering is given by Gebhart (1993).

OPCs tend to heat aerosols leading to a decrease in size and an increase in refractive index for hygroscopic atmospheric particles. These perturbations make it difficult to accurately measure atmospheric aerosol size distributions with OPCs, and insufficient attention is often given to these effects. Biswas et al. (1987) showed that these errors can be substantially reduced by using a heat exchanger to control the sheath air temperature within the OPC.

Instrument design and particle optical properties both play roles in determining the relationship between size and the pulse magnitude. Important instrument design features include characteristics of the illuminating radiation and the solid angle from which scattered light is collected and focused into the photodetector. Illuminating radiation is either monochromatic (laser) or incandescent (white light), and collecting optics of most commercial OPCs can be categorized as either near forward scattering or wide angle.

Both incandescent and monochromatic forward scattering instruments exhibit a monotonic dependence of pulse magnitude on size for very small particles. For nonabsorbing particles that are somewhat greater than the wavelength of the illuminating radiation, however, responses of both types oscillate with size, leading to nonmonotonic relationships between size and response. White light instruments that collect scattered light over a wide solid angle show a monotonic dependence of response on size for nonabsorbing particles. Monochromatic wide angle instruments exhibit oscillations for particles on the order of the wavelength of light and larger. For strongly absorbing particles, wide angle incandescent and monochromatic instruments exhibit a very weak dependence of pulse height on size for particle sizes between 0.3 and 1 μm .

Lasers provide illuminating intensities several orders of magnitude higher than can be achieved with incandescent sources, thereby enabling the detection of significantly smaller particles; laser OPCs having minimum detection limits of $\sim 0.05 \mu\text{m}$ are available, while white light OPCs typically cannot detect particles smaller than $\sim 0.3 \mu\text{m}$. Therefore, laser illumination is almost always preferable for particles smaller than the wavelength of the illuminating radiation, while white light illumination can have distinct advantages for larger particles (Gebhart et al., 1976). Nevertheless, most commercially available OPCs utilize laser illumination.

The angular distribution of scattered light for homogeneous spheres of known refractive index can be rigorously determined from theory (Mie, 1908). Numerous studies have shown reasonable agreement between the predictions of Mie theory and measured OPC responses for homogeneous spheres of known size and refractive index (Cooke and Kerker, 1975; Willeke and Liu, 1976; Garvey and Pinnick, 1983; Liu et al., 1985; Hinds and Kraske, 1986; Szymanski and Liu, 1986). For instruments that show the expected dependence of response on size, theory can be used to determine the relationship between response and size for particles having a refractive index different from the calibration aerosol. This approach is sometimes used for atmospheric measurements.

The challenge that arises when OPCs 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. For example, the aerosol may contain a mixture of particles consisting of homogeneous spheres, irregularly shaped solids, and solid seeds encapsulated by liquid droplets. 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.

To avoid such uncertainties, OPCs can be calibrated with atmospheric aerosols. Hering and McMurry (1991) used an electrical classifier to deliver

Los Angeles aerosols of known size and found that particles of a given size often produced two distinct pulse heights, indicating that two distinct types of particles were present. When this occurs, there is no unique relationship between pulse height distribution and size distribution. In this case such calibrations provide information that can be used to quantify measurement uncertainties. It is likely that particles in urban areas are more diverse than particles in remote regions and that OPC measurement uncertainties are therefore inherently more uncertain in urban areas.

Valuable information about the shape and/or refractive index of atmospheric particles can be inferred by measuring the angular distribution of scattered light (differential light scattering (DLS)). The multiangle aerosol spectrometer probe (MASP) (Baumgardner et al., 1993) measures the light scattered by individual particles for polar angles of 30–60° and 120–150°. If the particles are homogeneous spheres, then Mie theory can be used to infer refractive indices that are consistent with measurements. This instrument is being used routinely in aircraft measurements of atmospheric aerosols (e.g., Baumgardner et al. (1996)), and information on refractive index is being inferred from these measurements. Kaye and coworkers have developed several differential light scattering (DLS) instruments that provide information on shape for particles in the 1–10 μm diameter range (Kaye et al., 1991, 1996; Hirst and Kaye, 1996). Dick and coworkers (Dick et al., 1994, 1996; Sachweh et al., 1995) have used the DAWN-A (Wyatt et al., 1988) to measure azimuthal variabilities in light scattering so as to distinguish between spherical and nonspherical particles in the 0.2–2 μm range. The nonspherical fraction was found to be reasonably well correlated with the fraction of the aerosol that was of crustal origin and with the fraction of the aerosol that was “less hygroscopic” (Dick et al., 1998). These various studies illustrate the potential of DLS to provide valuable new information about properties of atmospheric aerosols.

In summary, while optical particle sizing techniques have been widely used for about 50 years, these techniques have evolved significantly in the past decade. Recent advances permit the detection of smaller particles, the calibration of optical detectors with optically complex atmospheric particles, and the measurement of particle properties such as shape and refractive index. It is likely that such advances will continue as digital signal processing techniques and laser technology evolve.

3.2.2. Aerodynamic particle size

When an aerosol is rapidly accelerated through a nozzle, 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. At least three commercial instruments are

available that utilize measurements of particle speed in an accelerating gas flow to determine size (Baron et al., 1993). These measured sizes are closely related to aerodynamic size. Because lung deposition and dry deposition of particles larger than 0.5–1 μm depend on aerodynamic size, data from these instruments provides direct information on such aerosol effects.

With these instruments, aerodynamic particle size is inferred from particle velocity, which is determined by measuring the time of flight between two illuminated volumes separated by a known distance (Dahneke, 1973; Dahneke and Padliya, 1977; Dahneke and Cheng, 1979; Remiarz et al., 1983; Mazumder et al., 1991). Unlike optical counters, which determine particle size from the intensity of the scattered light, these instruments simply use the scattered light to detect particles. This technique offers the advantage that measurements are not compromised by Mie resonances, which introduce complications in the interpretation of data from optical particle counters.

The aerodynamic diameter is defined as the diameter of a unit density sphere that has the same settling velocity as the particle (Hinds, 1982). Settling velocity is determined by a balance between aerodynamic drag and gravitational force. For most atmospheric particles, the Stokes's drag law can be used to determine the aerodynamic drag force on a settling particle. Stokes's law, however, applies only when the relative speed between the particle and the carrier gas is quite small (i.e., particle Reynolds Number $\ll 1.0$). Because particles are rapidly accelerated in these instruments, particle Reynolds numbers often exceed 1.0, especially for large particles. In this case non-Stokesian corrections must be made when determining aerodynamic size from measured particle velocities (Wang and John, 1987b; Ananth and Wilson, 1988; Cheng et al., 1990; Lee et al., 1990; Rader et al., 1990).

During the measurement of aerodynamic particle size, particles are expanded through a nozzle to a pressure that is well below atmospheric. The flow cooling and pressure drop associated with this expansion can lead to a change in relative humidity and may therefore affect measurements of particle size. Sizing errors also occur due to deformations in the shapes of liquid droplets (Baron, 1986). 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.

Measurement of aerodynamic particle size requires the optical detection of individual particles. The smallest reported size that can be measured with these instruments varies with instrument design and ranges from 0.2 to 0.5 μm . These instruments are capable of providing high-resolution information on aerodynamic size distributions in real time. Although they have seen only limited use for atmospheric measurements, such instruments have the potential to provide new and useful high-quality information in the future.

3.2.3. Electrical mobility analyzers

Electrical mobility analyzers classify particles according to the electrical mobility, Z , which for spherical particles is given by (e.g., Hinds, 1982):

$$Z = \frac{neC(D_p, P)}{3\pi\mu D_p}, \quad (8)$$

where n is the number of elementary charges carried by the particle, e is the magnitude of the elementary unit of charge, C is the slip correction factor (Rader, 1990), μ is the absolute gas viscosity, and D_p is particle diameter. Note that Z depends on gas properties, particle charge, and the geometric particle size but is independent of other particle properties such as density. Flanagan (1998) has written a comprehensive review of electrical aerosol measurements.

The first practical electrical mobility analyzer was developed by Kenneth Whitby and coworkers (Whitby and Clark, 1966). A refined design of the Whitby Aerosol Analyzer became a successful commercial product (the electrical aerosol analyzer or EAA (Liu et al., 1974)) and was used in some of the first measurements of ultrafine (particle diameter down to ~ 10 nm) urban aerosol size distributions (Whitby et al., 1972). In the EAA, particles flow through a unipolar charger, where they are exposed to small positive ions before entering the classifier. Particles having mobilities larger than a value determined by flow rates and the precipitating voltage are removed in the coaxial cylindrical classifier; all particles that are not precipitated are collected in a Faraday cup. Currents delivered to the Faraday cup are measured as a function of the precipitating voltage to obtain size distributions. Unipolar charging is used to deliver the maximum possible charge to the particles so as to maximize the current delivered to the Faraday cup.

The EAA has been largely replaced by the differential mobility particle sizer (DMPS; Keady et al., 1983). The DMPS includes a differential mobility analyzer (DMA, also referred to as the electrostatic classifier) (Liu and Pui, 1974a,b; Knutson and Whitby, 1975) and a particle detector (typically a CNC, but aerosol electrometers are occasionally used). Systems of this type can measure size distributions in the 3–500 nm diameter range. The DMA is the heart of the DMPS. In the DMA, the aerosol is first exposed to a bipolar cloud of ions, where it achieves Boltzmann charge equilibrium (Liu and Pui, 1974a,b; Adachi et al., 1983; Wiedensohler, 1988; Reischl et al., 1996). The mean charge of particles leaving the charger is close to zero, but a fraction of the particles contain ± 1 , ± 2 charges, etc. The contribution of multiply charged particles increases with increasing size. Particles in a narrow mobility range determined by the classifying voltage and flow rates are separated from

the main flow and delivered to the detector. The relationship between the measured concentration in the narrow mobility slice and the inlet size distribution is well defined (Knutson, 1976; Hoppel, 1978; Fissan et al., 1983). The complete size distribution is obtained by carrying out measurements at a number of classifying voltages. The deconvolution procedure used to determine inlet size distributions requires accounting for the multiple sizes associated with singly-charged, doubly-charged, etc., particles that are obtained at each classifying voltage (e.g., Hagen and Alofs, 1983).

The DMPS typically requires about 20 min to measure size distributions. The measurement time is determined by the time required for concentrations to stabilize after the classifying voltage is changed and the time required to achieve a statistically significant sample. Flagan and coworkers (Wang and Flagan, 1990) showed that measurement times can be reduced to ~ 2 min by ramping the classifying voltage continuously. Instrument systems that use this approach are referred to as scanning electromobility spectrometers (and also scanning mobility particle spectrometers – SEMS or SMPS). Voltage scanning is now typically used in measurements of atmospheric aerosol size distributions.

The most common geometry for DMAs involves annular flow through coaxial cylinders, as originally described by the Minnesota group (Liu and Pui, 1974a; Knutson and Whitby, 1975). An alternative cylindrical design that offers advantages in flow stability at high flow rates was developed by Reischl and coworkers in Vienna (Winklmayr et al., 1991). Electrostatic classifiers that involve radial flow between a pair of flat, parallel circular discs have been independently developed recently by two groups (Pourprix and Daval, 1990; Zhang et al., 1995).

The transport of particles through DMAs is unaffected by diffusion for particles larger than ~ 50 – 100 nm. This leads to a particularly simple expression for the probability that particles in this size range will exit with the “monodisperse” exit flow (Knutson and Whitby, 1975). This size-dependent probability is referred to as the “DMA transfer function”, and having an accurate expression for this transfer function is essential for determining size distributions from measured concentrations of classified particles. Diffusion leads to depositional losses during transport to, through and beyond the DMA, and it also leads to a broadening of the range of sizes that are carried by the classified aerosol flow. Quantitative investigations into the effect of particle diffusion in DMAs were first reported by Kousaka et al. (1985, 1986) and by Stolzenburg (1988). More recently, an extensive analysis of ultrafine particle classification by DMAs has been carried out in a collaborative activity between Chen and Pui of the University of Minnesota and Fissan and coworkers at the University of Duisburg (Chen and Pui, 1995; Fissan et al., 1996) and at the University of Leipzig in preparation for ACE-1

measurements (Birmili et al., 1997). The Duisburg/Minnesota collaboration led to the development of a detailed numerical model for particle transport through DMAs and to experimental measurements of DMA transfer functions for DMAs of various designs. An objective for this work has been to extend accurate measurements of size distributions with DMAs to sizes approaching 3 nm, where diffusion has a significant effect. A newly designed nanometer DMA was recently reported to minimize particle diffusional losses and diffusional broadening (Chen et al., 1996), and Fernandez de la Mora and coworkers have shown that the detrimental effects of diffusion can be largely eliminated for the Vienna-type DMA if minor design modifications are incorporated that permit operation at high flow rates (Rosell-Llompart et al., 1996; Seto et al., 1997; de Juan and Fernández de la Mora, 1998).

The primary limitation of DMPS/SMPS systems at the small particle limit is detecting very low concentrations of very small particles. Although CNCs can measure very low concentrations, their lower detection limit is presently ~ 3 nm. Aerosol electrometers can detect arbitrarily small particles, but cannot detect currents below $\sim 10^{-16}$ A, corresponding to a number concentration of ~ 40 cm $^{-3}$ at a typical sampling rate of 1 LPM. Concentrations of nanometer aerosols downstream of DMAs are often below this because the classified particles include only the charged fraction ($\sim 1\%$ at Boltzmann charge equilibrium for 3 nm particles) of particles in a narrow size range. A strength of SMPS/DMPS systems for sub 10 nm particles is that measurements are not affected by multiple charging. Thus, there is a unique relationship between the electrical mobility of classified particles and size.

Multiple charging is a primary limitation of SMPS/DMPS systems at the high end of the size spectrum. Large particles of a given mobility contain one, two, three or more elementary charges, each charge state corresponding to a different size. This increases the difficulty of deconvoluting the data to determine the contribution of each size to measurements at a given classifying voltage.

SMPS/DMPS instruments are clear improvements over the EAAs of 20 years ago and are without question the best available technique for measurement of size distributions between ~ 8 and 200 nm. Outside this range, these systems can still be excellent, depending on aerosol concentrations and size distributions, but other techniques that offer distinct advantages also require consideration. Measurement accuracies are likely to be size-dependent, and will be affected by particle shape. The accuracy with which these systems can measure atmospheric aerosol size distributions is difficult to quantify due, in part, to the lack of polydisperse aerosol standards.

3.2.4. Diffusion batteries

Particle diffusivities increase with decreasing size. Therefore, as particle sizes decrease, the rate at which they deposit on nearby surfaces increases. Diffusion batteries use this size-dependent deposition rate to obtain information on size distributions. They are most commonly used for particles smaller than $0.1\ \mu\text{m}$, because diffusion coefficients in this size range are high enough to lead to appreciable deposition rates. In the most commonly used diffusion batteries, the aerosol flows through a series of fine capillaries (Gormley and Kennedy, 1949; Sinclair, 1972) or fine wire-mesh screens (Sinclair and Hoopes, 1975a,b; Cheng and Yeh, 1980). Particles deposit on the inner surfaces of the capillaries or on the outer surfaces of the screens. Typically, a series of capillaries or screens is used, and the aerosol number concentration is measured downstream of each collecting element. Data for the decay in aerosol concentration through this series of collecting elements can be mathematically “inverted” to obtain the size distribution (Knutson et al., 1988; Ramamurthi and Hopke, 1989; Wu et al., 1989; Cooper and Wu, 1990; Reineking et al., 1994; Knutson, 1995).

Diffusion batteries are rugged, simple and are well suited for use in hostile environments, such as in-stack sampling. They have been used extensively for measurements of nanometer-sized radon progeny, since sensitive radioactive counting techniques can be used to measure the activity of ultrafine particles deposited on the particle collection surfaces. However, there are significant limitations to the quality of data that can be obtained with this approach. Because diffusion is a stochastic phenomenon, a wide range of sizes deposits on each collecting element. Thus, there is no simple relationship between the change in aerosol concentration across a collecting element and particle size. Furthermore, because size distributions are obtained from measurements of the change in concentration as the aerosol flows through the battery, measurements are adversely affected by other phenomena that cause change, such as shifts in the size distribution of the sampled aerosol. Finally, Cheng and Yeh (1980) showed that for screen-type diffusion batteries, two sizes of particles larger than $\sim 0.1\ \mu\text{m}$ can be collected with the same efficiency since interception and impaction become important collection mechanisms in addition to diffusion. Thus, in this size range there is not a unique relationship between size and collection efficiency. This leads to ambiguities in measured size distributions.

Diffusional separation has been largely superseded in recent years by electrostatic classification, which provides higher sizing resolution for most measurements of sub- $0.1\ \mu\text{m}$ atmospheric aerosol size-distributions. Nevertheless, diffusional separation offers benefits that will ensure its use for limited applications in the foreseeable future.

3.2.5. CNC pulse height analysis (PHA)

Recent work has shown that useful information about size distributions in the 3 to 10 nm diameter range can be obtained by measuring pulse height distributions produced by a steady-flow CNC operating in the single-particle-counting mode Saros et al. (1996). While particles larger than 10–15 nm all grow to about the same final droplet size in the CNC condenser, final droplet sizes decrease with initial particle size for smaller particles. This is due to the effect of curvature on equilibrium vapor pressure (Thompson, 1871): smaller particles must travel farther into the CNC condenser before they are exposed to sufficiently high supersaturations for condensation to occur. Therefore they have less time to grow. Recent work has shown that measured pulse height distributions can be mathematically inverted to determine the size distribution (Weber et al., 1998).

The PHA technique does not provide sizing resolution comparable to that obtained with SMPS (scanning mobility particle spectrometer) systems. However, it offers the advantage that every particle entering the CNC provides a signal. In contrast, only the charged fraction of the selected mobility fraction is detected with the SMPS. Because the charged fraction can be very small ($\sim 1\%$ for particles of 3 nm) and because measurements require scanning through a range of mobilities, the time required to acquire a statistically significant number of counts with the SMPS is significantly longer. The PHA technique offers significant benefits for studies of nucleation in the remote troposphere, where concentrations are low and changes can occur quickly (Weber et al., 1998). It is especially well suited for aircraft measurements.

3.3. Aerosol water content

Water comprises more than 50% of the fine particle mass at relative humidities exceeding 70–80% (e.g., Hänel, 1976; Zhang et al., 1993). The aerosol water content is determined by particle composition and relative humidity, and the amount of water in particles rises sharply above relative humidities of $\sim 80\%$. Most ionic species such as sodium chloride, sulfates, and nitrates are hygroscopic. Recent work (Saxena et al., 1995; Saxena and Hildemann, 1996; Dick, 1998) has shown that organic compounds may also significantly affect the aerosol water content.

One approach for determining particulate water content is to use thermodynamic models to calculate the aerosol water content (e.g., Pilinis et al., 1989) based on the measured composition of the major particulate species. A limitation of this approach is that current thermodynamic models do not account for water associated with organics. More quantitative information on concentrations of the major organic species and their hygroscopic properties

is needed before they can be incorporated into such thermodynamic models.

Ho et al. (1974) determined the liquid water content of atmospheric particles by using microwave resonance to measure the dielectric constant of samples that were collected on glass fiber filters. Their measurements showed that water mass content ranged from $\sim 10\%$ at 50% RH to 40% at 70% RH. Their instrument was unable to make measurements at relative humidities above 70%. An attractive feature of this approach is that it has the potential to provide information semi-continuously.

Several investigators have measured particulate water content by using a sensitive microbalance to measure the sensitivity of mass to relative humidity for particles collected on filter or impactor substrates (Winkler and Junge, 1972; Thudium, 1978; Hänel and Lehmann, 1981; Hitzengerger et al., 1997). Because relatively long times are required for deposits to equilibrate and because a specially designed relative-humidity controlled microbalance is required, this technique has seen only limited application. It does have the potential to provide accurate information.

Speer et al. (1997) used a β -gauge to infer the mass of particulate samples collected on 37 mm Teflon filters. They measured mass at relative humidities ranging from ~ 5 to 95% and determined the incremental water mass by difference. They found excellent agreement between β -gauge measurements and gravimetric measurements. Furthermore, the water mass uptake for ammonium sulfate measured with their instrument appears to be in good agreement with thermodynamic expectations. Although this technique has not been thoroughly studied, and while it is affected by the usual problems of all filtration techniques, it appears to offer promise as a practical technique for inferring water mass of atmospheric particles.

Lee and Hsu (1998) measured water in aerosol samples by using a thermal conductivity detector to measure the amount of water released by particles deposited on a filter upon exposure to pure helium. The detection limit for water was found to be 24 μg , and good agreement was found between measured water content and thermodynamic predictions for sodium sulfate and ammonium sulfate.

The tandem differential mobility analyzer (TDMA) (originally referred to as the "aerosol mobility chromatograph" (Liu et al., 1978)) has also been used to infer water content. This instrument system involves the use of two DMAs operated in series (Rader and McMurry, 1986). The aerosol classified by the first DMA is humidified or dehumidified between the DMAs, and the second DMA measures the effect of humidity on particle size (McMurry and Stolzenburg, 1989; Covert et al., 1991; Svenningsson et al., 1992, 1994). TDMA data can provide information on variations in water uptake among particles of a given size. TDMA measurements have shown that when atmospheric particles

of a given size are brought to high humidity, they often separate into two distinct types, which have been termed “more” and “less” hygroscopic. Based on comparison with known materials, it is found that measured growth factors are typically accurate to within 2%.

Because number concentrations of particles larger than about 0.5 μm are too low to permit TDMA measurements, all atmospheric data reported to date applies to smaller particles. Also, while the TDMA provides accurate information on the dependence of size on relative humidity, it does not provide direct information on particulate water mass concentrations. TDMA data can be used together with size distribution data, however, to obtain estimates of humidity-dependent mass concentrations. The TDMA has provided valuable insights into hygroscopic properties of atmospheric aerosols, but due to its high cost and complexity it is likely to remain a research tool rather than a monitoring device.

In summary, water is a significant component of atmospheric aerosols, and its contribution to mass increases strongly with relative humidity above $\sim 70\%$. The tendency of water to rapidly evaporate or condense with changes in relative humidity affects measurements with most instruments discussed in this review, and measurements of aerosol water content can sometimes be used to correct data for such errors. While a variety of techniques to measure water have been proposed, most of them involve differencing and thus cannot detect bound or hydrated water. Furthermore, some of these techniques involve measurements of size change, while others involve measurement of mass. Inferring mass change from size change (or vice versa) requires information about relative humidity-dependent density, which is typically unknown. It would be ideal to have a chemical technique for measuring water, but the techniques discussed above have substantially advanced our understanding of aerosol water content.

3.4. Aerosol volatility

Aerosol volatilization has been used as an indirect method of inferring particle composition. For example, Brock et al. (1995) sampled in parallel with two CNCs, one of which was equipped with an inlet heated to 192°C. Laboratory measurements showed that the heated inlet volatilized 90% of the particles that were smaller than 0.04 μm and contained only H_2SO_4 and H_2O . Field measurements showed that in some locations significant differences were found between the two CNCs, while in other locations the measurements were similar. By coupling these observations with other information that was known about the measured aerosol, they were able to conclude that ultrafine particles containing primarily H_2SO_4 and H_2O were present at some locations. Clarke (1993) has used similar systems in aircraft to measure the ef-

fect of volatilization on measured number concentrations and size distributions.

It would obviously be far preferable to have direct measurements of aerosol composition rather than the indirect information that is provided by volatilization. However, volatilization measurements can be done in real time (it has a time response of seconds) with instruments that are compact and convenient to deploy in the field. Fast time response is especially important for aircraft sampling.

3.5. *Particle density*

Particle density is needed to convert aerodynamic sizes to geometric (Stokes) sizes and to establish the relationship between aerosol mass and volume concentrations. In practice, density is usually calculated from measured particle composition. However, uncertainties in aerosol composition and the thermodynamic properties of mixtures lead to uncertainties in calculated densities.

Several approaches have been used to measure densities of submicron atmospheric aerosols. Hänel and Thudium (1977) measured the mass of bulk samples with an electronic balance, and measured the volume of the same sample using a specially designed pycnometer. The reported accuracy for these density measurements was 2%. Because bulk samples were used, information about variations with size or among particles of a given size was not obtained. Measurements of aerosol chemical composition were not reported, so it was not possible to compare measured to expected values.

Stein et al. (1994) measured the density of atmospheric particles in the 0.06 to 0.18 μm diameter range using the DMA-impactor technique. A DMA was used to deliver monodisperse particles of a known electromobility equivalent size (which does not depend on density and which equals the geometric size for spherical particles) to an inertial impactor. The particles' aerodynamic size, which depends on density, was measured with the impactor. Particle densities were determined to within $\sim 4\%$ from the measured geometric and aerodynamic sizes. Densities calculated from measured aerosol composition were found to be $\sim 20\%$ lower than measured values; the reason for this discrepancy was not resolved.

In summary, only a few efforts have been made to measure the density of submicron particles. Additional work is required to ensure that density can be calculated from measured particle composition. Closure studies of this type are an essential ingredient in the development of experimentally verified thermodynamic models of aerosol properties.

4. Measurements of aerosol chemical composition

4.1. Off-line measurements

Measurements of particle composition typically involve the chemical analysis of deposited particles in a laboratory some time after sample collection. Filters are the most commonly used collection substrates, but a variety of films and foils have been used with impactors to collect size-resolved samples. Sampling times vary with ambient loadings, sampling rates, substrate blanks, and analytical sensitivities but typically vary from several hours in urban areas to a day or more under clean background conditions. In addition, several off-line techniques are available for analyzing the composition of individual particles.

A variety of sampling artifacts can affect the measured composition of the collected particle deposit relative to what was actually in the atmosphere. Volatilization of semivolatile compounds (compounds that are found in both the vapor and particulate phases) is known to be a significant source of error for species like ammonium nitrate and many organics. Volatilization can occur because of pressure drop in the sampler, which upsets the equilibrium between the deposited particles and the vapor, or due to changes in temperature, relative humidity or composition of the incoming aerosol during sampling. Artifacts associated with sampling transport and storage have also been reported (Chow, 1995). Evaporative losses of particulate nitrates have been investigated in laboratory and field experiments with filters and impactors (Wang and John, 1988). The laboratory studies involved parallel sampling of ammonium nitrate particles with a Berner impactor and a Teflon filter. Both samplers were followed by nylon filters to collect evaporated nitric acid. Losses from the impactor were 3–7% at 35°C and 18% relative humidity, and losses from the filter were 81–95% under the same conditions. This result (that evaporative losses from the filter exceeded those from the impactor) is consistent with theoretical predictions (Zhang and McMurry, 1993) and was borne out by measurements in Los Angeles where negligible losses of nitrates from the impactor were found. Because evaporative loss rates from a given substrate are determined largely by the equilibrium vapor pressure of the evaporating species (Zhang and McMurry, 1987), the relative effect of evaporative losses will be usually be higher in background areas where particulate concentrations are low or at higher temperatures where vapor pressures are higher.

The diffusion denuder method was developed for the measurement of such semivolatile compounds (Possanzini et al., 1983). With this approach, the vapor phase diffuses and sticks to a coated surface upstream of the particle filter. An adsorber is located downstream of the filter to collect material that evaporates from the deposited particles during sampling. The particle-phase concentration is determined from the loading on the filter and on the adsorber

following the filter. The gas-phase concentration is determined either by measuring the amount of vapor-phase material collected on the "denuder" surface upstream of the particle filter or by subtracting the total (filter plus adsorber) loadings obtained with undenuded and denuded samplers. Diffusion denuders have been used with excellent success to distinguish inorganic gas phase species such as nitric acid and ammonia and from their particulate forms (Shaw et al., 1982; Mulawa and Cadle, 1985; Eatough et al., 1986; Knapp et al., 1986; Hering et al., 1988; Keuken et al., 1988; Koutrakis et al., 1988; Klockow et al., 1989; Koutrakis et al., 1993).

Measurements show that evaporative losses of semivolatile organic compounds can be significant (Commins and Lawther, 1957; De Wiest and Rondia, 1976; Katz and Chan, 1980; Peters and Seifert, 1980; Galasyn et al., 1984; Marty et al., 1984; Eatough et al., 1990). Application of the diffusion denuder technology to semivolatile organic compounds is an active area of research and shows promise for this difficult measurement task (Lane et al., 1988, 1992; Eatough et al., 1993; Gundel et al., 1995; Lawrence and Koutrakis, 1996). Because there are a wide variety of semivolatile organic compounds with varying adsorptive properties, finding the ideal denuder coatings is a nontrivial task. Turpin et al. (1993) demonstrated an alternative diffusion separator for semivolatile organic compounds that does not need a denuder. Definitive field testing has not been carried out.

The adsorption of organic gases on quartz filters is another source of error when sampling particulate organic carbon. Cadle et al. (1983) found that when two quartz fiber filters were used in series, the amount of carbon collected on the second filter was at least 15% of that on the first filter. Because the particulate collection efficiency exceeded 99.9%, it was concluded that the signal on the second filter was due to adsorption of carbon-containing gases. McDow and Huntzicker (1990) found that quartz backup filters collected more organic carbon when they followed Teflon pre-filters than when they followed quartz pre-filters, presumably because quartz is more effective than Teflon at removing adsorbing vapors. McMurry and coworkers (McMurry and Zhang, 1989; McMurry et al., 1996a) have found that the amount of "organic carbon" found on the quartz after-filter following an impactor can be comparable to the amount of organic carbon collected on the impactor stages. Because measurements of physical size distributions show that very little particulate mass should be found below the 0.05 μm cut point of the bottom impactor stage, and because the absence of comparable amounts of sulfate on the after-filter suggests that particle bounce is not responsible for the observed high organic carbon loadings, it was concluded that the high after-filter loadings are due to gas adsorption.

These discussions of sampling artifacts illustrate the dismal state of the art for measurement of particulate organic carbon, which can comprise nearly

50% of the fine particle aerosol in the arid southwest and in regions like Denver and Los Angeles, which are heavily impacted by vehicular emissions. An understanding of the particulate organic composition will require improved sampling methodologies and more attention to speciation (Schauer et al., 1996).

4.1.1. Filter sampling

The most common approach for determining the composition of atmospheric aerosols involves the analysis of deposits collected on filter substrates. While filter samplers are inexpensive, they require manual operation. Furthermore, the number of filters that must be analyzed in a monitoring network or in an intensive field campaign can be large. For example, 60,000 filters were collected during the 1990 NGS visibility study, and their analyses contributed significantly to the cost of the \$14 million study (NRC, 1993).

Chow (1995) provides a comprehensive treatment of the use of filters to determine the chemical content of particulate matter. In this review she discusses suitable filter materials for various analytical methods, species sampling artifacts, and analytical techniques that can be used for various species. The discussion of analytical techniques includes a valuable comparison of sensitivities. The reader is referred to this paper for a discussion of this topic.

4.1.2. Impactors

Impactors are used to classify particles according to aerodynamic diameter. The aerodynamic diameter is defined as the diameter of the unit density sphere having the same settling speed as the particle. The relationship between aerodynamic diameter, D_a , and geometric diameter, D_p , for spherical particles is

$$D_a = D_p \left(\frac{\rho_p}{\rho_0} \right)^{1/2} \left(\frac{C(D_p)}{C(D_a)} \right)^{1/2}, \quad (9)$$

where the slip correction factor C (Rader, 1990) accounts for noncontinuum effects that become significant when particles sizes approach the mean free path of the gas. Thus, aerodynamic diameters exceed geometric diameters for particles with densities above 1 g cm^{-3} . Cascade impactors with a series of stages, each with a successively smaller cut point, are commonly used to collect size-resolved atmospheric samples for chemical analysis. 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.

The dimensionless parameter that determines whether particles are collected by an impactor is the Stokes number, St , defined as

$$St = \frac{\tau U_0}{D_{\text{nozzle}}/2} = \frac{\rho_p D_p^2 C U_0}{9\mu D_{\text{nozzle}}}, \quad (10)$$

where τ is particle relaxation time, U_0 is the mean velocity through the accelerating nozzle, D_{nozzle} is the diameter of the accelerating nozzle, ρ_p is particle density, D_p is particle diameter, C is the slip correction factor and μ is the absolute viscosity of the gas. Marple and coworkers (Marple, 1970; Marple and Willeke, 1976) developed design criteria for impactors that allow impactors to be designed with predictable cut points. In practice, impactors collect particles that have Stokes numbers larger than a critical value typically in the range 0.21–0.23.

Impactors that collect particles larger than a few tenths of a micron are straightforward to design and fabricate. Collecting particles smaller than this requires either the use of very small nozzles or low pressures (C increases as pressure decreases). Both of these approaches have been used, and impactors that collect particles down to 0.05 μm are now used routinely (Berner et al., 1979; Hering and Friedlander, 1979; Cahill and Malm, 1987; Marple et al., 1991). Because very little mass is associated with particles smaller than 0.05 μm , these impactors can collect virtually all of the particulate mass. Very small nozzle diameters are required to collect small particles, so multinozzle impactors are commonly used to achieve adequate sampling rates.

Particle bounce is an inherent problem with impactors. Coated substrates largely eliminate bounce and are commonly used for atmospheric sampling (Dzubay et al., 1976; Wesolowski et al., 1977; Lawson, 1980; Turner and Hering, 1987; Wang and John, 1987a; Pak et al., 1992). Measurements have shown that liquid oils tend to provide better bounce-prevention characteristics than do viscous greases. 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. An alternative approach involves sampling at elevated relative humidities, where submicron atmospheric particles typically contain enough liquid water to prevent bounce (Winkler, 1974). Stein et al. (1994) showed that bounce of small ($\sim 0.2 \mu\text{m}$) atmospheric particles is largely eliminated at relative humidities exceeding $\sim 75\%$.

A variety of impaction substrates have been used for sampling ambient aerosols with impactors. Aluminum foil is often used when samples are to be analyzed for organic and elemental carbon (OC/EC), since precleaning can reduce the carbon blanks in these substrates to very low levels. Carbon-free substrates are required since OC/EC analyses involve measuring the amount of CO_2 that is released when the samples and substrates are burned. Precleaned

Teflon or Mylar film is often used for ion chromatography analyses, since ion blanks can be made very low on such surfaces. Teflon membrane filters have also been used as impaction substrates. Although these are more costly than film or foil substrates, they do not require precleaning, and they are compatible with nondestructive analytical methods such as x-ray fluorescence analysis (XRF) or proton induced x-ray emission (PIXE).

4.1.3. *Laser microprobe mass spectrometry*

The analysis of individual particles by mass spectrometry has been reviewed in several papers (Spurny, 1986; McKeown et al., 1991; Noble et al., 1994). Laser microprobe mass spectrometry (LAMMS) (Wieser et al., 1980; de Waele and Adams, 1986; Kaufmann, 1986; Spurny, 1986; Artaxo et al., 1992) involves the off-line analysis of particles collected on a substrate. Particles are irradiated with a high-power pulse laser, and the ejected ion fragments are analyzed by mass spectrometry. LAMMS can detect trace levels of metals in individual particles at the parts-per-million level (Otten et al., 1987; Bruynseels et al., 1988a), can speciate inorganic compounds including nitrates and sulfates (Bruynseels and van Grieken, 1984; Bruynseels et al., 1988b; Ro et al., 1991), can detect trace organic compounds (De Waele et al., 1983; Mauney and Adams, 1984; Niessner et al., 1985), and can distinguish surface species from those contained within the particle (De Waele et al., 1983; Bruynseels and Van Grieken, 1985; Niessner et al., 1985; Bruynseels and Van Grieken, 1986; Wouters et al., 1988). Because LAMMS is an off-line technique that exposes particles to a vacuum environment before they are analyzed, particle composition can be altered by chemical reactions or evaporation before analysis. Also, because collected particles must be returned to the laboratory for analysis, there is typically a significant time delay before data are available.

4.1.4. *Electron microscopy*

Individual particle analysis by electron microscopy can provide information on particle morphology and elemental composition. With this approach, particles are collected on a filter or impaction substrate and are irradiated by electrons under vacuum conditions. Information on elemental composition is achieved by measuring the X-ray energy spectrum produced by interactions of the electrons with the particles. Windowless or thin-window detectors can detect X-rays from elements with atomic number 11 (sodium) and greater, and the location of elements on or within particles can be determined by using electron beams that are small relative to particle size. A review of the various electron analytical techniques for particles is given by Fletcher and Small (1993).

Electron microscopy has led to important discoveries concerning atmospheric aerosol chemistry. For example, Andreae et al. (1986) found that remote marine aerosols contained internal mixtures of silicates and sea-salt, which they attributed to cloud coalescence. Sheridan and coworkers (1994) found that particles consisting mostly of crustal species or soot are coated with sulfur when found in the lower stratosphere but not in the upper troposphere. McInnes and coworkers (1994) found evidence for the substitution of sulfate for chloride in sea-salt particles in marine atmospheres, and McMurry and coworkers (1996) showed that less hygroscopic particles in urban areas tended to consist of carbon-containing chain agglomerates, while more hygroscopic particles were rich in sulfur. Other researchers have used electron microscopy to categorize individual particles into groups that provided information on source categories (Linton et al., 1980; Kim and Hopke, 1988; Van Borm and Adams, 1988; Rojas et al., 1990; van Borm et al., 1990; Katrinak et al., 1995; Anderson et al., 1996b). Because these observations require data on the composition of individual particles, bulk analysis techniques could not have provided similar information.

A limitation of microscopic techniques is that obtaining data for a statistically significant sample can be extremely time consuming. To deal with this issue, several groups have developed automated systems that can analyze large numbers of particles (Casuccio et al., 1983; Anderson et al., 1988; Schwoeble et al., 1988; Artaxo et al., 1992).

Obtaining quantitative chemical information by X-ray microanalysis can also be problematic. Several researchers have proposed standardless techniques for obtaining quantitative elemental composition (Russ, 1974; Armstrong and Buseck, 1975; Janossy et al., 1979; Aden and Buseck, 1983; Wernisch, 1985; Raeymaekers et al., 1987). These techniques account for interactions of X-rays with neighboring atoms and, in some cases, particle shape. However, in measurements with monodisperse particles of 2,6-naphthalenedisulfonic acid, disodium salt ($C_{10}H_6(SO_3Na)_2$) ranging in size from 0.207 to 1.122 μm , Huang and Turpin (Huang and Turpin, 1996) found that standardless techniques led to compositional errors exceeding 78%.

The measurement of volatile species by electron microscopy is also problematic. Volatilization occurs because particles are exposed to vacuum conditions for extended times during analysis and because samples are heated by the electron beam (Gale and Hale, 1961; Almasi et al., 1965; Watanabe and Someya, 1970; Curzon, 1991; Huang, 1997). For example, nitrates, which tend to be relatively volatile, are usually not detected by X-ray analysis even though they are often present in significant quantities (McInnes et al., 1997). Similar losses of semivolatile organic compounds are likely. Several researchers have shown that volatilization loss rates of sulfuric acid droplets are much greater than loss rates of ammonium sulfate particles (e.g., Webber, 1986; Huang

and Turpin, 1996). 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 volatilization losses that occur in conventional electron microscopes. Huang and coworkers (1994) used the ESEM to observe in real time the effects of condensating and evaporating liquid water on diesel chain agglomerates on a substrate.

Selecting the optimal substrate for electron microscopic analysis is also an issue. Ideally, the substrate should contain no elements that will interfere with the analysis of atmospheric particles. Due to its low atomic weight, beryllium produces no interfering X-rays and thus might seem to be an ideal substrate for scanning electron microscopy. However, beryllium is impractical to handle due to its toxicity, and laboratory measurements have shown that acid sulfate particles are not detected on beryllium due to interactions between the particles and the beryllium (Huang and Turpin, 1996). Samples are often collected on carbon-containing membranes, leading to difficulties with the measurement of particulate carbon content. McInnes et al. (1997) found that particles on TEM grids must contain at least 30% carbon in order to measure the particulate carbon. There is no ideal substrate that is suitable for analysis of all major elements found in atmospheric particles.

In summary, despite the limitations outlined above, electron microscopy has provided valuable information on the composition, sources, and atmospheric transformations of atmospheric aerosols. Electron microscopy is the only individual particle technique that provides both morphological and compositional information on ultrafine particles, and samplers that are used to collect particles for electron microscopic analysis are typically relatively inexpensive and simple to operate. It is likely that electron microscopy will continue to be an important tool in the analysis of atmospheric particles for some time to come.

4.2. Real-time measurements

There is, at present, little readily available instrumentation for measuring the composition of aerosol species in real time. Laboratory prototype instruments have been developed for measuring particulate sulfur, nitrogen and carbon concentrations in the field on time scales ranging from minutes to hours, and these instruments are discussed below. Also, prototype versions of mass spectrometers that can determine the composition of individual particles in real time have recently been developed. 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.

4.2.1. Real-time particulate carbon analyzers

Turpin et al. (1990b) developed an automated instrument for in situ measurements of fine particle “organic” and “elemental” carbon with a detection limit of $0.2 \mu\text{gC m}^{-3}$. Sampling intervals vary with ambient concentrations; an interval of two hours was used for measurements in Los Angeles (Turpin and Huntzicker, 1995). Sampling involves parallel trains for collecting particles and for adsorbing organic vapors. Particulate samples (train 1) are collected on a quartz filter after coarse particles are removed with a $2.5 \mu\text{m}$ impactor. Because of the affinity of quartz for organic vapors, the particle filter also collects such vapors. Adsorbing vapors (train 2) are collected on a quartz filter located downstream of a Teflon filter that removes particles but presumably not organic vapors (McDow and Huntzicker, 1990). The particulate carbon concentration is obtained by subtracting the carbon concentration on train 2 from that on train 1. Samples are analyzed by sequentially heating the filters in trains 1 and 2, first in helium at 650°C to volatilize organic carbon. The gases that evolve from the heated filters are converted to CO_2 in a MnO_2 catalyst at 1000°C and then to CH_4 in a nickel-firebrick methanator at 500°C . The methane is detected using a flame ionization detector. Elemental carbon concentrations are then obtained by measuring the carbon-containing gases that evolve when the particulate filter (train 2) is exposed to a 2% mixture of O_2 in He and ramped from 350 to 750°C .

An ambient carbon particulate monitor is available commercially (Rupprecht et al., 1995). In this instrument, sub- $10 \mu\text{m}$ particles are collected at 16.7 l m^{-1} with a multi-jet impactor having a $0.14 \mu\text{m}$ aerodynamic diameter size cut. The impactor can be operated at temperatures ranging from ambient to 150°C , and sample collection times can be adjusted from 1 to 24 h. The particulate carbon content is determined by measuring the amount of CO_2 that is produced in a 750°C afterburner when the collected particles are heated in air. “Organic” carbon is determined from the amount of CO_2 that is produced when the aerosol sample is heated to 340°C , and “soot” is determined from the amount of CO_2 that is produced when the aerosol sample is heated to 750°C . The manufacturer reports the instrument resolution to be $\pm 0.25 \mu\text{g m}^{-3}$ at 1σ and 1-h collection. This instrument is probably less affected by adsorption artifacts than samplers that rely on quartz filters since the surface area of the impaction substrate is much smaller than that of filters. Sources of measurement error include evaporative losses, pyrolysis of the sample which may lead to an overestimate of the “soot” concentration, and omission of particles smaller than $0.14 \mu\text{m}$, which will lead to an underestimate of the true particulate carbon content. Measurements with MOUDI impactors in Los Angeles (Zhang et al., 1993), in Meadview, AZ (McMurry et al., 1996b), and in the Great Smoky Mountain National Park (Vasiliou and McMurry, 1997) showed that the frac-

tions of the particulate carbon associated with particles smaller than $0.18\text{ }\mu\text{m}$ were 0.14 ± 0.19 , 0.22 ± 0.06 and 0.18 ± 0.08 , respectively. Based on these results it can be concluded that roughly 20% of the carbon-containing particulate matter is not collected by the $0.14\text{ }\mu\text{m}$ impactor of this carbon analyzer.

4.2.2. Real-time particulate sulfur and nitrogen species analyses

Several groups have reported techniques for in situ measurements of particulate sulfur concentrations. Many of these techniques involve the use of flame photometric detectors (FPD) (Coburn et al., 1978; Huntzicker et al., 1978; Kittelson et al., 1978; Tanner et al., 1978, 1980; D'Ottavio et al., 1981; Garber et al., 1983; Allen et al., 1984; Slanina et al., 1985). The FPD detects $\sim 394\text{ nm}$ light given off by excited-state S_2 molecules formed when sulfur compounds are burned in a hydrogen-rich flame. Although the FPD was originally intended for measurements of gaseous sulfur compounds, research has shown that it also detects particle-borne sulfur. The response times of the FPD instruments for particulate sulfur are as low as $\sim 1\text{ min}$, and the minimum detectable limits are typically $\sim 1\text{ }\mu\text{g m}^{-3}$.

Because the FPD responds to both gaseous and particulate sulfur, particles and gases are usually separated before they enter the hydrogen-rich flame. For measurements of sulfur-containing gases, the sample flows through a filter prior to entering the flame. For particulate sulfur measurements, the interfering gases are usually removed with a denuder. An alternative approach developed by Kittelson et al. (1978) and Keady (1987) permits simultaneous measurements of gases and particles. It uses an electrostatic precipitator cycling at about 0.2 Hz ; only gases are measured when the precipitator is on, while both gases and particles are measured when it is off.

Measurements of sulfate speciation with the FPD have been reported. Speciation is achieved by heating the aerosol to preset temperatures upstream of the particulate sulfur monitor. Several studies have shown that temperatures of 71 , 142 , and 190°C , respectively volatilize sulfuric acid, ammonium sulfate salts, and refractory sulfur species (Huntzicker et al., 1978; Kittelson et al., 1978; Tanner et al., 1980). Allen et al. (1984) report that sulfuric acid can be removed from sulfate salts if the aerosol is preheated to a temperature of 120°C before entering the FPD. The volatilized components are typically removed by a denuder, and the remaining aerosol is then measured by the particulate sulfur monitor. Species concentrations are determined by difference.

Jaklevic et al. (1981a) developed an automated sampler in which particulate sulfur concentrations were determined by X-ray fluorescence (XRF) analysis. This latter system has a minimum detectable limit of $0.1\text{ }\mu\text{g m}^{-3}$ for sampling periods of $\sim 1\text{ hour}$. A comparison of particulate sulfur measurements by five FPD instruments and the XRF instrument of Jaklevic et al. was carried out in

St. Louis in August, 1979 (Camp et al., 1982). This study showed that measurements of all samplers were well correlated, and four of the six instruments in the study agreed to within $\pm 5\%$ on average.

Suh et al. (1994) compared measurements of sulfate concentrations obtained with their FPD instrument (the CSTS-continuous sulfate/thermal speciation system) with values obtained using the Harvard/EPA annular denuder system (HEADS) and a Micro-Orifice Impactor (MOI). They found that the CSTS was well correlated with the integrating samplers and provided concentrations that agreed with the other samplers to within experimental uncertainty.

Despite these encouraging results, such instruments are not widely used. Instrument calibrations are sensitive to relative humidity and to pressure, and obtaining accurate measurements at low ambient concentrations requires constant surveillance by a knowledgeable operator. Additional development would be required before an instrument of this type could be reliably deployed for routine monitoring.

Stolzenburg and Hering (1999) recently developed a system for measuring particulate nitrate concentrations. Particles are collected with a single stage impactor that is $>95\%$ efficient for particles larger than $0.1 \mu\text{m}$ aerodynamic diameter, and the sampled aerosol is humidified to prevent bounce in the impactor. Collected particles are analyzed by flash vaporization using a chemiluminescent NO_x analyzer. Measurements in Southern California showed good agreement with data from a denuded filter sampler. Deposits containing 5 ng of nitrate can be analyzed, corresponding to a detection limit of $0.7 \mu\text{g m}^{-3}$ for 8 min samples collected at 1 l m^{-1} . The detection limit is due to variabilities in the blank and could be reduced by if a source of more consistent blanks were developed.

Ion chromatographs (ICs) have also been adapted to semicontinuous measurements of particulate and gaseous species. Simon and Dasgupta (1995a) used an IC to analyze the effluent from a parallel plate wet denuder to determine concentrations of gas-phase nitrous (HONO) and nitric (HNO_3) acids. Detection limits for HONO and HNO_3 were 110 and 230 ppq , respectively. Particulate sulfate, nitrite, and nitrate were collected with a vapor condensation aerosol collection system and analyzed by IC. Detection limits for 8-min sampling intervals were, respectively, 2.2 , 0.6 and 5.1 ng m^{-3} (Simon and Dasgupta, 1995a,b). Khlysiou et al. (1995) reported detection limits of $0.7 \mu\text{g m}^{-3}$ for ammonium, sulfate, nitrate, and chloride particles that were collected by steam condensation and analyzed with an automated IC system. Buhr et al. (1995) combined a wet denuder for nitric acid with a pyrex frit for particle collection to determine HNO_3 vapor and particulate nitrate and sulfate. Zellweger et al. (1999) modified the method of Dasgupta and coworkers to reduce interference from NO_2 . Karlsson et al. (1997) used a single-stage impactor to collect particles larger than $0.4 \mu\text{m}$ onto a wetted substrate for semicontinu-

ous analysis of sulfate and nitrate by IC; this methodology could be adapted to real-time measurements of size-resolved ionic composition. Because these approaches are amenable to the simultaneous measurement of semivolatile gases and particulate species, provide information on a number of species, and provide relatively good time resolution for typical ambient concentrations, they show promise for the future.

4.2.3. Real-time single-particle mass spectrometry

Several groups have developed real-time in-situ techniques for the analysis of individual particles in a flowing gas stream by mass spectrometry. This technique involves rapid depressurization of the aerosol, formation of a particle beam, and irradiation of particles by a high-power pulse laser to produce ions that are analyzed by mass spectrometry. Early work on this technology was reported by Stoffels and Lagergren (1981), by Sinha et al. (1982), Sinha and Friedlander (1985), Giggy et al. (1989), Marijnissen et al. (1988) and McKewen et al. (1991). Within the past five years this technology has been advancing rapidly, largely through innovations by several groups in the US and Europe (Thomson and Murphy, 1993, 1994, 1997; Hinz et al., 1994, 1996; Mansoori et al., 1994; Noble et al., 1994; Nordmeyer and Prather, 1994; Kievit, 1995; Murphy and Thomson, 1995; Reents et al., 1995; Salt et al., 1996). This approach offers most of the capabilities of LAMMS and avoids some of its limitations. Real-time instruments have been shown capable of providing information on surface coatings (Carson et al., 1997a, b), multicomponent crystallization (Ge et al., 1996), compound speciation (Neubauer et al., 1996), and oxidation state (Neubauer et al., 1995). Although particles must be brought into a vacuum before they can be analyzed, the time at reduced pressure is typically ~ 1 ms, which is short enough to avoid losses of most semivolatile compounds, although some loss of water is likely. Also, because particles are analyzed in real time, these instruments are well suited for studying time-dependent phenomena or for use on aircraft.

Within the past several years, single-particle mass spectrometers have been used in field measurements of atmospheric aerosols in Düsseldorf, Germany, in the Rocky Mountains, in Los Angeles and at Cape Grim, Australia. Each of these field campaigns has provided important new information about properties of atmospheric aerosols. For example, Hinz et al. (1994, 1996) found that principal component analysis could be used to identify the major chemical components of the primary particle types, thereby providing information on particle source categories. Murphy et al. (1997a, b) found that in the Rocky Mountain aerosols, sulfate and nitrate usually (but not always) occur in different particles and that organics occur in most particles. Prather and coworkers (Noble and Prather, 1996; Liu et al., 1997) were able to identify pyrotechnically derived

particles following July 4th fireworks, and they also demonstrated the ability of their instrument to resolve size/composition correlations for atmospheric particles. Finally, Murphy and coworkers found that at Cape Grim, Australia (Middlebrook et al., 1998; Murphy and Thomson, 1997c, 1998), most sulfate-containing particles down to $0.16\text{ }\mu\text{m}$ also contained some sea salt, indicating that sea salt may provide the seeds on which cloud condensation nuclei form in this region, that organics were commonly internally mixed with sea salt, and that halogens in individual particles were anti-correlated with sulfates, suggesting that the halogens were displaced by sulfates as the particles aged.

Most of the real-time instruments currently under development measure particle composition with time-of-flight mass spectrometry. Depending on particle size, however, various approaches are used to trigger the pulse laser and to measure particle size. For particles larger than about $0.2\text{ }\mu\text{m}$, particles are usually detected as they flow through a volume illuminated by a low-power continuous wave (cw) laser. The scattered light is used to trigger the high-power pulse laser to volatilize and ionize the particles. The instruments of Hinz et al., Murphy et al., Johnston/Wexler et al., and Marijnissen et al. also use the intensity of scattered light from the cw laser to obtain an estimate of particle size. In the instrument of Prather and coworkers, the time of flight between two low-powered cw laser beams separated by a known distance is used to measure particle velocity, which is used to infer aerodynamic size. Sizes obtained from particle velocity are more accurate than those obtained from the intensity of scattered light. Particles smaller than $\sim 0.2\text{ }\mu\text{m}$ cannot easily be detected by light scattering. Nevertheless, Reents et al. (1995) and Carson et al. (1997a,b) have had success at detecting particles as small as $\sim 0.01\text{ }\mu\text{m}$ by firing the pulse laser at the maximum possible rate. Although particles are irradiated for only a small fraction of the laser pulses and although only a small fraction of the particles are present when the laser is fired, useful information on the composition of individual ultrafine particles has been obtained in this way. These measurements do not provide direct information on size. However, by using a differential mobility analyzer Liu and Pui (1974a, b) to deliver particles of known size, Carson et al. (1997a, b) were able to determine the size and composition of ultrafine (sub $0.2\text{ }\mu\text{m}$) particles.

An alternative approach for real-time analysis of size-resolved aerosol composition by mass spectrometry was reported by Jayne et al. (1999). They collect size-segregated particles on a filament that is heated to vaporize and ionize the deposited particles by electron impact. Ions are detected using a quadrupole mass spectrometer. They report that their technique can be used to measure the composition of particles as small as 5 nm diameter. Because all particles in a specified size range are collected on the filament, this approach has a higher detection efficiency for ultrafine particles than other approaches that have been

reported. Their instrument can detect either individual particles or an ensemble of particles.

In summary, the real-time compositional analysis of particles by mass spectrometry has advanced rapidly in the past five years. In the coming years, instruments of this type will provide fresh insights into particle sources, chemical transformations between particles and gases, and the distribution of species among, on, and within particles. Although most measurements to date do not provide quantitative information on mass concentrations, recent work has provided some encouragement that obtaining quantitative mass concentration may be possible (Jayne et al., 1996; Gross et al., 1997).

5. Calibration of atmospheric aerosol instrumentation

A review of techniques used to produce calibration aerosols is given by Chen (1993). In this section the techniques that are most commonly used to calibrate atmospheric aerosol instrumentation are discussed. Significant progress has been made since 1970 in the development of techniques for generating calibration aerosols, but the measurement of atmospheric aerosols introduces challenges that are not all resolved by these tools.

As was mentioned in the introduction, measured particle “sizes” depend on physical-chemical properties such as shape, density, refractive index, and geometric size, depending on the measurement method. The techniques described below can be used to produce laboratory calibration aerosols of known size and with known physical-chemical properties. However, atmospheric aerosols are often hygroscopic and typically contain mixtures of species and phases. Furthermore, properties such as shape, density and refractive index of atmospheric particles are typically not known with high accuracy. Therefore, it is not possible to produce synthetic particles that accurately mimic all qualities of atmospheric particles. These differences in properties of calibration and atmospheric aerosols introduce measurement uncertainties that are often difficult to quantify.

One approach that can reduce measurement uncertainties is to calibrate instruments with atmospheric particles. This can be done by using a DMA (see below) to select atmospheric particles of known electrical mobility equivalent diameter. For spherical particles (most but not all submicron atmospheric particles are spherical), the electrical mobility equivalent diameter equals the geometric size. Thus, this approach can provide a reasonably good measure of the relationship between instrument response and particle geometric diameter. Significant ambiguities remain, however, even when an instrument is calibrated directly with atmospheric particles. For example, it is known that atmospheric particles of a given size often vary in composition. Therefore, an unambiguous

relationship between size and properties does not exist. Furthermore, the water content of hygroscopic particles varies with relative humidity. Therefore, refractive indices and densities also vary with relative humidity. The response of an OPC depends on refractive index, and responses of aerodynamic size classifiers depend on density, so calibrations of such instruments done at one relative humidity will be invalid when the relative humidity changes. Furthermore, the dependence of refractive index and density on relative humidity is not well known, so it is not straightforward to correct data for changes in properties that occur when relative humidities change.

The challenge of calibrating aerosol instruments is greater for instruments that significantly alter the thermodynamic environment of the aerosol. For example OPCs tend to heat the aerosol and aerodynamic particle sizers and impactors expand the aerosol through nozzles, both of which lead to changes in relative humidity and therefore particle size. It is somewhat easier to control the temperature in electrostatic classifiers, so these instruments are less prone to such errors.

Improving the accuracy of atmospheric aerosol measurements will require more attention to physical-chemical properties that affect instrument response, and this should remain a goal of atmospheric aerosol research. Only when it is possible to reconcile measurements made with different methods will we be able to refine our understanding of measurement accuracy.

5.1. Polystyrene latex spheres

Monodisperse polystyrene latex (PSL) and polyvinyl toluene (PVT) spheres ranging in size from 0.01 to 30 μm suspended in dilute liquid solutions are available from a variety of commercial sources. Monodisperse calibration aerosol particles are produced by atomizing the liquid solutions into a fine mist and evaporating the solvent. A fraction of the mist droplets contain a PSL or PVT sphere, and these spheres provide a useful calibration aerosol.

PSL and PVT spheres are well characterized with respect to size and composition and are inexpensive and relatively easily to generate in the laboratory. One difficulty is that the atomized liquid always contains a small amount of nonvolatile solute. Therefore, atomized droplets that do not contain a PSL or PVT sphere produce a small "residue" particle (Whitby and Liu, 1968). The concentration of these residue particles is typically much higher than the concentration of the larger PSL or PVT particles. Therefore, in some applications it is necessary to remove the residue particles before the atomized aerosol can be used for calibration. This is most often accomplished by electrostatic classification.

5.2. *Electrostatic classification by the differential mobility analyzer (DMA)*

Differential mobility analyzers (DMAs; for more information see section on electrical mobility analyzers) can be used to produce calibration aerosols of known size (~ 1 –500 nm), concentration and composition. They can also be used to select monodisperse slices of “unknown” aerosols such as atmospheric aerosols for use in instrument calibration or for studies of aerosol properties. Size is determined from its known dependence on electrical mobility, classifying voltage and flow rates (Knutson and Whitby, 1975). Careful measurements have shown that the mean size exiting a DMA agrees with theory to within $\pm 3\%$ (Kinney et al., 1991). DMAs are typically operated under conditions that lead to a size range of $\sim \pm 10\%$, although this can be adjusted within limits. Concentration is determined by collecting charged particles at the exit from the DMA on a filter housed within a Faraday cage (Liu and Pui, 1974a,b). By using a sensitive electrometer to measure the current delivered to the filter, the charge delivery rate is obtained. If particles are singly charged, the concentration equals this charge delivery rate divided by the volumetric flow rate through the filter. Composition is determined by the composition of aerosols entering the DMA. It is often relatively easy to generate polydisperse aerosols of known composition by atomizing known liquid solutions or by nucleating and condensing known vapors, etc.

Multiple charging complicates the use of DMAs for producing calibration aerosols, and it becomes more problematic as particle size increases. Multiple charging leads to a multiplicity of sizes at a given classifying voltage, which is clearly a problem if one's objective is to determine the response of an instrument to particles of a known size. Multiple charging also leads to errors in measurements of aerosol concentrations using the aerosol electrometer, since multiply charged particles deliver more than a one elementary charge to the electrometer. Several schemes for eliminating multiply charged particles from DMA-produced aerosols have been published. Romy-Novas and Pui (Romy-Novas and Pui, 1988) used an impactor to remove multiply charged particles, and Gupta and McMurtry (Gupta and McMurtry, 1989) used a specially designed charger that produced few multiply charged particles. Despite these limitations, the DMA is one of the most versatile calibration tools due to its wide dynamic range and due to its ability to select particles of known size from any aerosol.

5.3. *Vibrating orifice aerosol generator*

A vibrating orifice aerosol generator (VOAG) (Berglund and Liu, 1973) can produce monodisperse particles when solutions containing a known concentration of a nonvolatile solute are forced through a very small orifice (5 to 20 μm

diameter) at a known volumetric rate. The orifice is connected to a piezoelectric crystal that vibrates at a known frequency. This vibration delivers a regular instability to the liquid jet leaving the orifice, thereby causing the liquid to break into uniform droplets of known size. When the solute evaporates, a non-volatile particle of known size remains. In principle, the particle production rate equals the crystal oscillation rate, thereby opening the possibility that the VOAG could be used to produce aerosols of known concentration as well as size. In practice, the VOAG is not often used as a concentration standard since it is difficult to avoid some deposition losses of the relatively large droplets produced by the vibrating orifice. Another problem that is encountered with VOAG aerosols is that droplets can collide, leading to particles that contain an integral number of primary droplets. The effect of collision can be minimized by adjusting the VOAG operation until the number of multiplets detected with an aerodynamic particle sizer is negligible.

VOAGs can produce monodisperse particles ranging in diameter from 0.5 to 50 μm . Obtaining particles smaller than 1.0 μm is difficult since it is difficult to avoid plugging of the very small orifices that must be used. Particle sizes are uniform to within about $\pm 1.4\%$.

6. Federal reference method

The original National Ambient Air Quality Standard (NAAQS) for particulate matter was for "total suspended particulate matter" (TSP) and was in force from 1970 to 1987, when it was replaced by a standard for particles smaller than 10 μm aerodynamic diameter (PM_{10}) (Register, 1987). More recently, an additional fine particle ($\text{PM}_{2.5}$) has been proposed (Register, 1997). These methods are briefly reviewed in light of the preceding discussion on measurement methodologies.

The PM_{10} standard defines performance specifications of PM_{10} samplers. Particles smaller than 10 μm are inertially separated from larger particles. The sampler "cut point" is defined such that the aerodynamic size for which 50% of the particles is collected falls in the 9.5–10.5 μm diameter range. The sampling efficiency increases to $\sim 100\%$ for smaller particles and drops to 0% for larger particles. Particles are collected on filters, and mass concentrations are determined gravimetrically. Measurement precision for 24-h samples must be $\pm 5 \mu\text{g m}^{-3}$ for PM_{10} concentrations below $80 \mu\text{g m}^{-3}$, and 7% above this level. Sample volumes are adjusted to sea level pressure and 25°C .

Provision is made for "reference" and "equivalent" measurement PM_{10} methods. Reference methods meet all of performance specifications including those cited above. "Equivalent" methods may involve collection or analysis methods different from those defined by the PM_{10} standard, yet which can be

shown to perform equivalently based on specified side-by-side comparisons with an approved reference method sampler. Several beta-gauge instruments and a harmonic oscillating element instrument have been certified by EPA as PM₁₀ equivalent methods.

The new Federal Reference Method for determining mass concentrations of sub-2.5 μm particles (PM_{2.5}) was published in the Federal Register on July 18, 1997 (Register, 1997). In contrast to the PM₁₀ performance specification, this PM_{2.5} FRM specifies all details of the sampler design and of sample handling and analysis. The sampler consists of a PM₁₀ inlet, an oil-soaked impaction substrate to remove particles larger than 2.5 μm , and a 47 mm polytetrafluoroethylene (PTFE) filter with a collection efficiency exceeding 99.7% for particle collection. The sampling duration is 24 h, and the sampler temperature is to not to exceed ambient values by more than 5°C. Filters are weighed before and after sampling at relative humidities in the 30% to 40% range and controlled to within $\pm 5\%$. Mass measurements at relative humidities down to 20% are permissible if the mean ambient relative humidity during sampling is less than 30%. The description of the PM_{2.5} reference method in the Federal Register acknowledges that "because the size and volatility of the particles making up ambient particulate matter vary over a wide range and the mass concentration of particles varies with particle size, it is difficult to define the accuracy of PM_{2.5} measurements in an absolute sense . . . Accordingly, accuracy shall be defined as the degree of agreement between a subject field PM_{2.5} sampler and a collocated PM_{2.5} reference method audit sampler. . ."

The FRM also provides for Classes I–III equivalent methods for PM_{2.5}. Class I equivalent methods use samplers with relatively small deviations from the sampler described in the FRM. Class II equivalent methods include "all other PM_{2.5} methods that are based on a 24-h integrated filter sampler that is subjected to subsequent moisture equilibration and gravimetric mass analysis." Class III equivalent methods include filter-based methods having other than a 24-h collection interval or non-filter-based methods such as beta attenuation, harmonic oscillating elements, and nephelometry.

The strength of the PM_{2.5} FRM is that because the sampler design is specified in complete detail, measurements at all locations should be comparable. In light of the previous discussion, however, several limitations can be identified. The oil-soaked impaction substrate requires maintenance to ensure that it does not become caked with deposits of coarse particles since this could lead to particle bounce and cause fine particle concentrations to be artificially inflated. It is not always safe to assume that such maintenance will be carried out, especially in routinely operated sampling networks. Furthermore, the oil-soaked impaction substrate must collect all particles between 2.5 and 10 μm . If an inlet with a smaller size cut were used, the delivery of soil dust to the 2.5 μm impactor could be substantially reduced, thereby reducing the required main-

tenance frequency. Another concern is that transfer of oil or organic vapors from the oiled frit could contaminate the filter, thereby precluding analysis of organics on archived filters.

Both the PM₁₀ and PM_{2.5} standards are defined with consistency rather than accuracy in mind. We know, for example, that evaporative losses of species including ammonium nitrate and organics will lead to a significant underestimate of the true fine particle mass concentration in some locations. If measurement techniques were developed that eliminated such systematic errors, they could not be certified as either reference or equivalent techniques because they would not agree with data from the reference method samplers.

7. Summary of significant advances

- Instrumentation for producing laboratory calibration aerosols of known size, composition and concentration became available about 25 years ago. This instrumentation is now widely used to characterize the response of aerosol instrumentation to known aerosols. These calibration techniques have facilitated a steady advance in the quality of atmospheric aerosol measurements.
- Mass spectrometers that can measure the composition of individual atmospheric particles in real time are now available. These instruments open a new set of questions that can be addressed regarding sources and reactivity of atmospheric aerosols, and may evolve to techniques for routine, real-time measurement of aerosol chemical composition.
- Methods for routine, real-time measurement of size distributions of aerosols in the 3 nm to > 10 μm are now available.

8. Summary of future aerosol measurement needs

- Gravimetric techniques that are used for regulatory compliance purposes involve filtration. While such methods are relatively simple and inexpensive to implement, they require manual operation, provide only rough time and spatial resolution, and are subject to sampling errors that cannot be quantified. Real-time techniques for accurate measurement of mass that avoid such sampling errors are needed.
- The response of aerosol instruments depends on particle properties including density, complex refractive index and shape. More information on such properties is required to improve our understanding of measurement accuracy.

- Instrumentation to measure aerosol composition in real time is needed. Most analytical measurements are done off-line and are expensive. While some effort has been made to measure particulate sulfur, carbon and nitrate concentrations in real time, the instruments that have been developed are mostly laboratory prototypes and would require further development if they were to be used for routine measurements. It is possible that individual particle mass spectrometry will evolve into instruments that can provide accurate real-time data of size resolved composition, but more work is needed to evaluate the potential of these instruments for such measurements.
- The measurement of particulate carbon-containing species is especially problematic. While aerosols include many carbon-containing species with a wide variety of chemical and thermodynamic properties, most measurements crudely identify these as either “elemental” or “organic carbon”. There is no standard analytical technique that is accepted as the “correct” method for distinguishing between elemental and organic carbon, so different laboratories often obtain different results for the same sample. Furthermore, substantial sampling errors are encountered, especially for organic carbon. It is likely that significant progress on measurements of the carbon-containing portion of particles will require more attention to speciation.
- Water is a major component of the aerosol, and is the most abundant fine particle species for relative humidities exceeding $\sim 80\%$. An accurate, real-time technique for measurements of aerosol water concentration is needed.
- Our understanding of particle surface composition and the distribution of chemical species and phases within individual particles is poor. Chemical interactions between particles and gases are almost certainly affected by particle surface composition, and transformations within particles must depend on details of particle makeup. The development of instrumentation to provide such information would provide fresh insights into chemical reactivities of atmospheric aerosols.
- Our understanding of chemical interactions involving atmospheric particles is primitive relative to our understanding of purely gas-phase chemistry. This is due, in large part, to the fact that chemists have historically played a secondary role to physicists and engineers in aerosol science. Many of the challenges for the future are chemical, and recent work shows a rapid increase in the sophistication with which aerosol chemistry is treated. It is likely that this trend will continue.
- Nucleation is an unsolved problem in aerosol science. Nucleation occurs in combustors that produce primary pollutant emissions and in the atmosphere as a result of chemical transformations. Understanding the chemical and physical processes that lead to the birth of new particles by nucleation will require information on the composition and concentration of the molecular clusters that serve as their precursors. “Bridging the gap” between mole-

cles and macroscopic (> 3 nm) particles remains a challenge to the scientific community.

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