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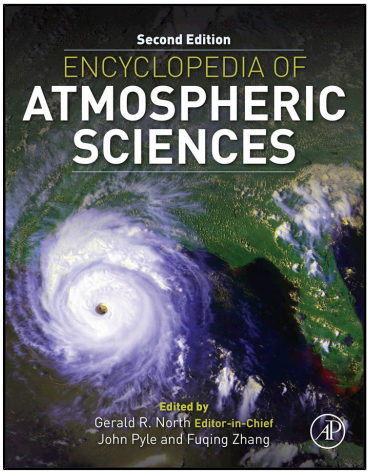


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# Observations for Chemistry (*In Situ*): Particles

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## Synopsis

The principles behind the large suite of instruments available for *in situ* particle observations are described. Instruments use condensation, optical scattering, electrical mobility, direct capture, absorption, and dissociation to provide highly resolved space and time measurements of aerosol number, size, mass, composition, optical properties, shape, and nucleating characteristics, when a full suite of instruments is available. Such measurements are required to fully characterize and understand the role of particles in certain aspects of heterogeneous chemistry, radiative transfer, cloud formation, and precipitation.


## Introduction

### History

The scientific observation, and discovery, of particles or liquids suspended in air, or aerosol, began with Tyndall in the 1850s through his observation of forward scattering from particles in direct sunlight. This led to Tyndall's further investigation of smaller particles by dark field microscopy, establishing the basis for nephelometers, ultra microscopes, and optical particle counters. At nearly the same time the work of Epsy, Coulier, and Aitken led to the realization that particles were required for the condensation of water in air and that this could be used to measure concentration, leading to condensation particle counters. Human interest in aerosol significantly preceded these discoveries, due to the obvious impact of aerosol on life through air pollution: the foul air of Rome, coal burning in London, mortality of hard rock miners. Thus, the first concerted measurements of aerosol, in the early 1900s, were focused on high concentrations of respirable particles which, when captured in alveoli, will lead to various forms of emphysema, depending on the contaminant particles: silicosis, tabacosis, and asbestosis. The natural role of particles in the formation of droplets and ice crystals in clouds, and their possible use in cloud seeding, was apparent by the end of the 1940s. The pivotal role of aqueous particles in mediating the atmospheric concentrations of reactive trace gases, in particular stratospheric ozone, became apparent in the 1980s. The interaction of particles with radiation was described well by the early 1900s; however, the impact of aerosol on the Earth's radiation balance has only recently been of significant interest as we strive to understand, and forecast, the impact of the increasing atmospheric abundance of carbon dioxide on the Earth's future. As the twenty-first century begins, the measurement of aerosol particles appears even more important than at the beginning of the twentieth century, when measurements began.

### Aerosol Characteristics

The instruments and tools available today to measure aerosol are impressive: filters, electron microscopy, condensation particle counters, optical particle counters, nephelometers, mobility analyzers, impactors, mass spectrometers, lasers, fast microprocessors, and ample storage facilities. The task, however, is more impressive and no instrument can provide all the information desired. Atmospheric aerosols arise from the Earth's surface, through combustion, mechanical disturbance, and gas to particle conversions from gaseous organic and volcanic emissions. Particle sizes range from $<1$ nm to $>10$ μm, concentrations from $>10^4$ cm$^{-3}$ for small particles to $<10^{-3}$ cm$^{-3}$ for large particles, and mass concentrations from $<1$ μg m$^{-3}$ to $>1$ mg m$^{-3}$. Particle shape varies and particles may be externally or internally mixed (Figure 1). Tropospheric particles contain a large fraction of the nonnoble elements in the upper half of the periodic table (Figure 2). The most common volatiles are water, organics, nitrates, sulfates, and ammonium. The most common crustal materials are aluminum, silica, and iron oxides. Aerosol particles provide cloud condensation and ice nuclei. Removal occurs through sedimentation and cloud processes. Residence times are typically $<30$ days in the troposphere, less than atmospheric mixing times, leading to large spatial and temporal structure. Stratospheric aerosols are well mixed, within a few years of penetrating volcanic eruptions, with residence times of years.

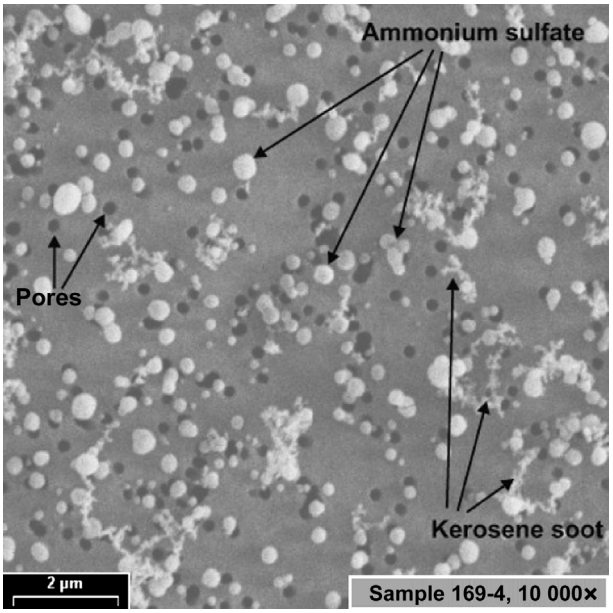


**Figure 1** Electron micrograph of externally mixed ammonium sulfate and soot particles. From Sheridan, P., Arnott, W., Ogren, J., et al., 2005. The Reno aerosol optics study: an evaluation of aerosol absorption measurement methods. Aerosol Science and Technology 39, 1–16. Copyright 2005. Mount Laurel, NJ. Reprinted with permission.



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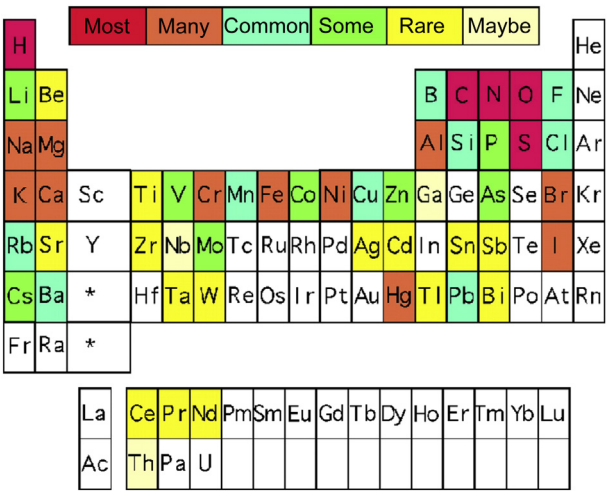


**Figure 2** Elements observed in aerosol particles above 5 km. Frequencies are approximate because of differing ionization efficiencies, isotope signatures, and spectral interferences. From Murphy, D.M., Thomson, D.S., Mahoney, M.J., 1998. *In situ* measurements of organics, meteoritic material, mercury, and other elements in aerosols at 5 to 19 kilometers. Science 282, 1664–1669. Reprinted with permission from AAAS.

To completely characterize atmospheric aerosol would require time and space-resolved measurements of aerosol number, size, mass, composition, optical properties, shape, charge, and nucleating characteristics. No instrument is capable of this; however, individual *in situ* instruments and techniques are available which can measure each of these properties relying on condensation, optical scattering, electrical mobility, direct capture, and dissociation. *In situ* implies measurements at or in the immediate vicinity of an instrument. *In situ* aerosol measurements provide highly resolved space and time measurements, while suffering from severely limited space and time coverage, which are more easily obtained from remote aerosol measurements, such as lidar, limb extinction, or other electromagnetic-radiation-based sensors. *In situ* measurements, however, offer the only way to describe some of the specifics of aerosol populations required to fully characterize/understand heterogeneous chemistry, radiative transfer, cloud formation, and precipitation. *In situ* measurements play vital roles in improving our understanding of each of these fundamental areas.

### Uncertainties

*In situ* instruments measure either an ensemble of particles or single particles, and are either extractive or noninvasive. Extractive instruments pull aerosol samples into a sampling chamber, while noninvasive instruments define a sampling volume external to the instrument, generally optically. Ensemble instruments are sensitive to the entire size distribution at once and thus measure directly integrals of the size distribution: mass, surface area, composition, absorption, scattering, or extinction. Single particle measurements provide size distributions of most of these quantities, and nucleating characteristics. Extractive instruments provide a larger suite of properties and are required for particles $<0.5$–$1.0$ μm. All extractive instruments suffer from biases due to the inlets and tubing leading to the sampling chamber. An ideal inlet has an internal air speed matching the speed of air flowing past the inlet, is straight, not too long, and does not heat the sample. As real inlets deviate from the ideal they may over- or under- count the edges of the size range; may lose particles in the inlet tube due to turbulent, inertial, electrostatic, or diffusional impaction; and particle size may change due to evaporation. Noninvasive instruments are required for particles $>10$ μm, and are generally used for cloud particles. The illuminated volume defines the sample volume. Uncertainties arise from particles at the sample volume edge and from fragments of particles broken on the shrouds for the optical source and detector. Aside from uncertainties introduced by the inlet, or sample volume, all instruments have additional sampling biases related to sensitivity to specific size ranges, number concentrations, mass concentrations, and ionization thresholds. Each specific instrument has its own calibration and sampling efficiency challenges, and not all can be fully met, leading to instrumental limitations for many applications; see approximate size limitations in Figure 3. Adequate descriptions of these challenges and limitations cannot be accomplished here and will not be attempted. Instead the general principles underlying the instruments used to measure the wide array of aerosol properties will be focused on. The article will be organized around these aerosol properties. Table 1 summarizes the instruments and properties measured.

Although some aerosol sampling techniques, such as microscopy, spectroscopy, and gravimetry, provide primary data and are thus self-calibrating, most aerosol instruments require calibration against primary standards. Once instrument response functions are established partial calibrations are usually adequate for routine operation. The most fundamental primary standard is electron microscopy, for nonvolatile particles. Commercial primary standards include polystyrene latex beads of specific single sizes and aerosol generation and classification systems capable of supplying reliable monodisperse aerosol samples between 0.01 and 1.0 μm for several aerosol compositions. Sample flow rates must also be carefully measured. However, even with careful calibration, the precision of most aerosol measurements is 20% or more, significantly higher than most gas phase measurements. The reason for this has less to do with the maturity of the instrumentation, than the complexity of aerosol particles compared to gas molecules. For gases, molecular composition, structure, size, shape, and mass are mostly well known. The primary measurement is concentration, and, at levels of parts per trillion, the number concentration of molecules exceeds total aerosol populations by factors of a thousand or more. Thus counting uncertainties are small. For aerosol particles counting uncertainties are large and are dominant for the largest particles, none of the properties listed above are known a priori, and often the particles are not well mixed so particle shape and composition will vary among the particles sampled, Figures 1 and 2, in addition to the normal variations in size and mass.

## Chemical Properties

### Composition

Aerosol mass spectrometers provide the biggest advances in the past 20 years for aerosol composition measurements. These

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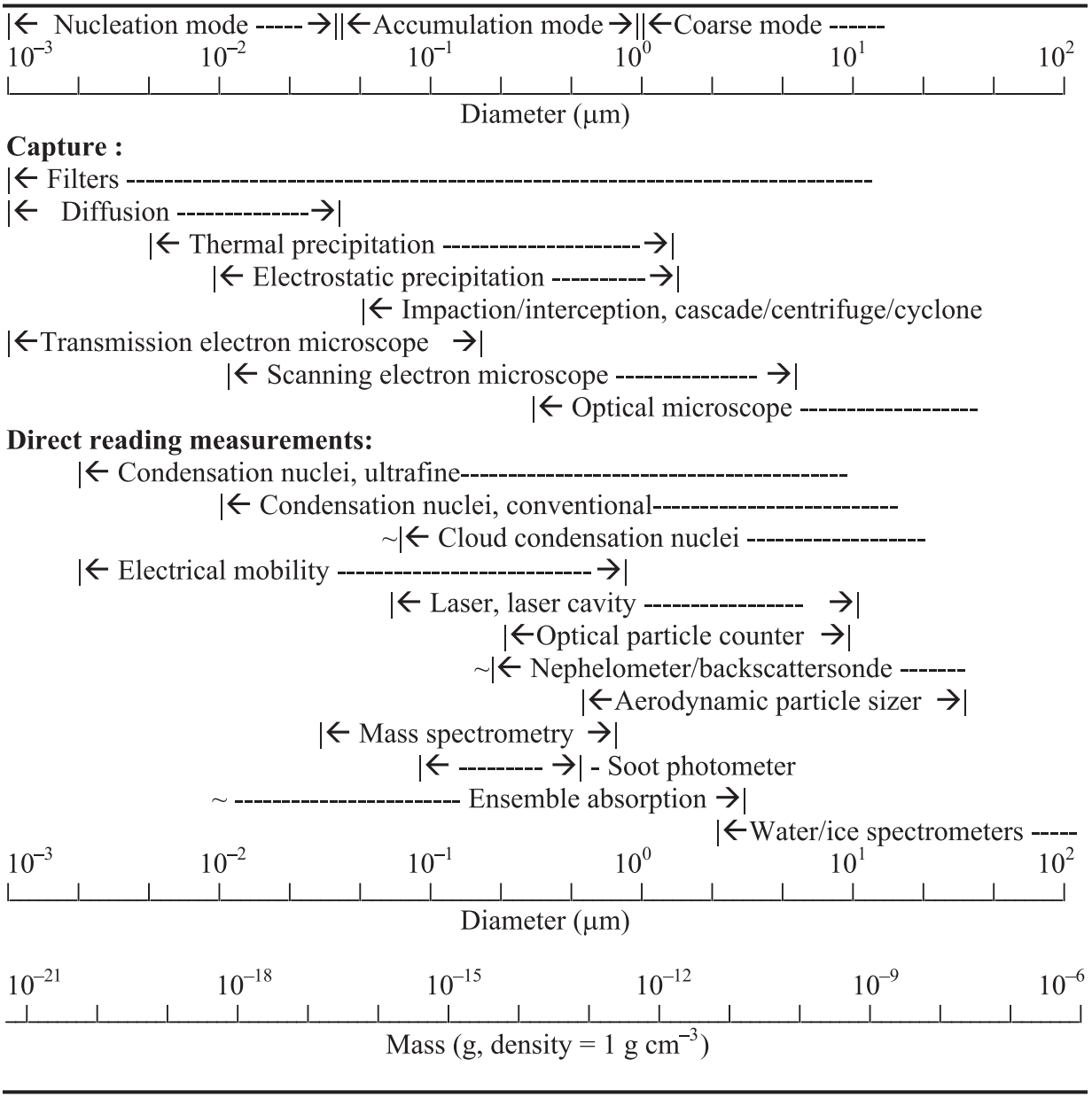


**Figure 3** Size range for *in situ* aerosol measurement techniques as a function of diameter (μm). Interdecadal divisions on the log scales are at approximately 2 and 5. The size range for the nucleation, accumulation, and coarse modes typically assumed for atmospheric aerosol are shown at the top. Particle equivalent mass for a density of 1 g $cm^{-3}$ is shown at the bottom.

single particle extractive instruments size and chemically analyze individual aerosol particles in real time, and several commercial instruments are available. Prior to this capability nearly all the chemical information was based on postanalysis of captured particles. Mass spectrometers consist of an evacuated inlet, which focuses particles into a central beam, a size determination, particle volatilization and ionization, and a mass to charge (m/z) detector, Figure 4. The differences in these pieces define the different aerosol mass spectrometers available. Inlets may consist of single orifices, capillaries, or aerodynamic lenses, with the latter two capable of focusing a range of particle sizes. An aerodynamic lens is a series of decreasing orifices, with each orifice concentrating successively smaller particles onto the central beam and is most common. Sizing is accomplished through either optical scattering or time of flight from the inlet exit to the target. Volatilization is accomplished by heating or laser ablation. Heating vaporizes only the volatile components, whereas laser ablation also provides refractory components. The vaporized molecules are ionized by electron impact, photoionization, or chemical ionization. The efficiency of ionization determines the quantitative nature of the measurement. Electron impact and chemical ionization are more well characterized, leading to more quantitative mass fractions when used. In contrast

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**Table 1** Aerosol properties measured by *in situ* aerosol instruments

| | *Physical properties* | | | | | *Chemical properties* | | | *Optical properties* | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *Instrument* | *Mass* | *No.* | *Size* | *Shape* | *SA* | *Crustal/elements* | *Volatile/ions* | *Carbon* | *Scat* | *Abs* | *Ext* |
| **Captured particles** | | | | | | | | | | | |
| Gravimetry/microbalance | X | | | | | | | | | | |
| Microscopy | I | X | X | X | | | | | | | |
| Colorimetry | | | | | | X | X | | | | |
| X-ray fluorescence | | | | | | X | | | | | |
| γ-Ray emission | | | | | | X | | | | | |
| Atomic spectroscopy | | | | | | X | | | | | |
| Ion chromatography | | | | | | | X | | | | |
| Infrared Raman spectroscopy | | | | | | | X | | | | |
| Mass spectrometry | | | | | | X | X | | | | |
| Oxidation | | | | | | | | X | | | |
| **Direct reading single particle** | | | | | | | | | | | |
| Condensation nuclei | | X | | | | | | | | | |
| Cloud condensation/ice nuclei | | X | | | | | | | | | |
| Electrical mobility | I | X | X | | I | | | | | | |
| Optical particle counter | I | X | X | | I | | | | I | | |
| Soot photometer | | X | X | | | | | X | | I | |
| MS-laser ablation/ionization | I | X | X | | | X | X | | | | |
| MS-volatilization, EI ionization | I | X | X | | | | X | | | | |
| **Direct reading ensemble** | | | | | | | | | | | |
| Nephelometer/backscattersonde | | | | | | | | | X | | |
| Aethalometer | | | | | | | | | | X | |
| Photoacoustic spectrometer | | | | | | | | | | X | |
| Cavity ring-down spectrometer | | | | | | | | | | | X |
| Epiphaniometer | | | | | X | | | | | | |

MS, mass spectrometer; EI, electron ionization; SA, surface area; X, property measured; I, property implied; Scat, scattering; Abs, absorption; Ext, extinction.

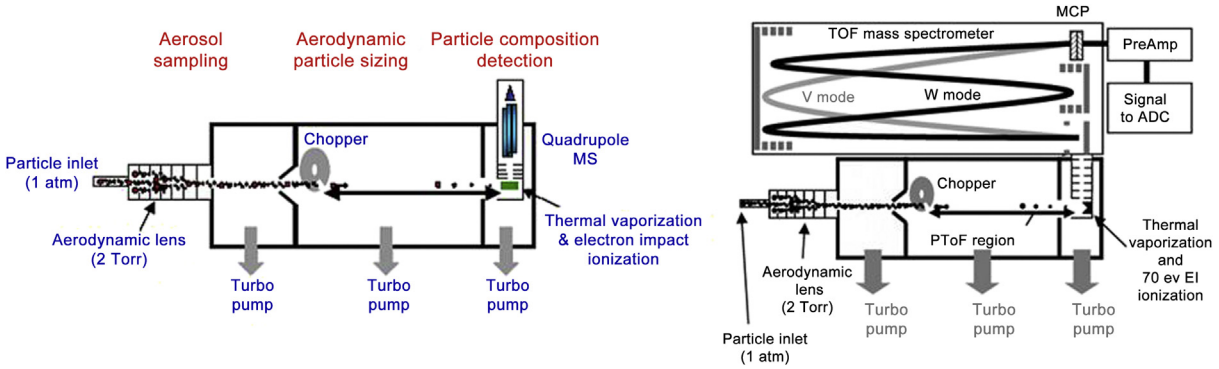


**Figure 4** Schematic diagrams of two aerosol mass spectrometers showing an aerodynamic focusing lens, vaporization and ionization region, and mass spectrometer. The mass spectrometer on the left is a quadrupole and on the right a time of flight using reflector plates to produce either a V or W charged particle path. The figure on the left is reproduced with permission from M.L. Alexander, EMSL, Richland, Washington. The figure on the right is reprinted with permission from DeCarlo et al., Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer. Analytical Chemistry 78, 8281–8289. Copyright 2006 American Chemical Society.

photoionization leads to less quantitative results. The ion detectors are primarily either quadrupole or time of flight. Quadrupole detectors focus ions of specific m/z ratios onto the electron detector. Only one m/z ratio can be sampled per particle due to timing limitations. Scanning through the m/z ratios for a series of particle impacts provides a quantitative mass spectra. Time of flight spectrometers use an electric potential to accelerate ions into a drift tube ending at the electron detector. The spectrum of arrival times provides the mass spectrum since the drift velocity is mass dependent. The drift tube may be straight or bent to increase the length and thus resolution.

Prior to the advances in aerosol mass spectrometry chemical information was primarily limited to chemical analysis of particles captured on filters and more recently in high purity water. These ensemble invasive techniques can determine the elemental, ionic, and carbonaceous composition of aerosol, and are the only possibility for some applications. Elemental

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analysis is accomplished by colorimetry, X-ray fluorescence, γ-ray emission, or atomic emission or absorption spectroscopy. Elemental concentrations are identified by spectroscopy of absorption or emission lines. Colorimetry uses wet chemistry to produce a solution whose light absorption is quantified. X-ray fluorescence and γ-ray emission use an energy dispersive detector to measure characteristic X-rays or γ-rays emitted from excited states of the elements. X-ray fluorescence is induced by exposure to X-rays or protons, γ-ray emission by exposure to neutrons. For emission and absorption spectroscopy, samples are dissolved and vaporized. Atoms excited by arcs, inductively coupled plasmas, sparks, or lasers will emit. Alternatively absorption of radiation by samples dissociated into ground state atoms in a flame can be measured.

Ions such as, $SO_4^{2-}$, $NO_3^-$, and $NH_4^+$, major components of ambient aerosol, can be measured by colorimetry, ion chromatography, selective ion electrodes, infrared or Raman spectroscopy, or mass spectrometry. The first three techniques measure only the aqueous fraction of the aerosol. Ion chromatography, most widely used, separates sample ions within a column using ion exchange. Ion concentrations are measured with conductivity. Particle into liquid samplers inject the aerosol into a region of high water supersaturation forcing water to condense on the aerosol. The water droplets containing the aerosol are collected and inorganic ion fractions determined with ion chromatography. To remove gaseous contaminants the aerosol stream is usually preceded with a denuder.

Infrared or Raman spectroscopy uses infrared photons at energies characteristic of molecular vibrational bands, which are absorbed in proportion to molecular concentration. Visible photons, which inelastically (Raman) scatter from samples display frequency shifts characteristic of molecular vibrational bands. These techniques are also sensitive to organics and oxidized organics. For mass spectrometry, a laser volatilizes and ionizes the collected samples, or an ion beam removes, 'sputters,' ions off particle surfaces. Ion detection then proceeds as described above.

### Carbon Content

Measurement of carbon in aerosol is another area with recent significant advancement, while remaining particularly challenging, due to the thousands of organic species, plus black carbon, which appear in particles. Mass spectrometers provide measurements of the volatile organics, but laser ablation is required for black carbon. Specific black carbon instruments are invasive and range from ensemble filter, cavity ring down, and photoacoustic, to single particle absorption. Total carbon can be determined by oxidizing filter samples and measuring the $CO_2$. Techniques to separate total carbon into elemental and organic are attempted; however, there is no accepted standard. Techniques include slowly volatilizing organics or graduated chemical extraction. All other techniques rely on the absorption of light by carbon. Continuous measurements of light absorption by aerosol collected on filters provide good relative values but have large uncertainties. Cavity ring-down spectrometers trap photons in a sample chamber with highly reflective mirrors. Light intensity decays as the light is absorbed and scattered by the ensemble of particles in the cavity. The decay time then measures aerosol extinction of the light. To obtain absorption requires an independent measure of scattering. Photoacoustic spectrometers measure absorption directly by measuring the acoustic waves resulting from heating of aerosol in the sample cavity by the absorption of light. The laser source is modulated at a characteristic frequency of the sample cavity, thus amplifying the sound for detection. The single particle soot photometer measures the incandescent black body radiation from particles, which are vaporized within the cavity of an infrared laser. Only absorbing particles will absorb the laser energy and become heated, with the time to vaporization, and the temperature, dependent on the carbon content. Particle size is measured simultaneously by scattering. This technique can be combined with mass spectrometric measurements of the incandesced particles for more detail.

### Index of Refraction

Index of refraction is a function of aerosol composition, and if particle molar ratios are known, index of refraction can be derived. Another approach is to use size distribution measurements to calculate scattering for comparison with scattering measurements. The index of refraction is used to match the calculated and observed scattering. There have been a few attempts to measure particle index of refraction directly using optical instruments with detectors at several angles. Changes in index of refraction will lead to dissimilar changes in angular scattering, which should be sensible. These multiangle approaches have not proven to be very robust.

## Physical Properties

### Concentration

The first measurements of number concentration, the tyndallometer, and ultramicroscope were limited to particles large enough to scatter visible light, approximately $>0.3$ μm, which misses the majority of aerosol. These instruments, however, were quickly followed by Aitken's condensation nuclei (CN) counter, variations of which remain the standard technique for number concentration. All CN counters consist of a saturator, condenser, and detector. The working fluid, water, butanol, and ethylene glycol, is evaporated into the aerosol stream in the saturator. Supersaturation occurs in the condenser and is achieved with either expansive or conductive cooling. Expansive cooling and water were originally used to create a cloud, which attenuates a light beam; however, none of these original instruments remain in service. Today, continuous flow instruments with conductive cooling supersaturation chambers are used. Typically air is saturated with *n*-butyl alcohol, at temperatures near 30 °C, before entering the condenser, held near 0 °C, where the air becomes rapidly supersaturated. Each particle acts as a condensation site and becomes a droplet large enough to be detected optically. The extent of supersaturation, controlled by the temperature difference between saturator and condenser, determines the minimum particle size, which will be condensed upon and thus be counted. Size distributions can be measured by preselecting particles with a diffusion battery or differential mobility analyzer, or by carefully controlling the supersaturation to activate successively smaller particles. An alternate total concentration measurement can be accomplished by charging

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the aerosols with unipolar ions and then measuring the current as the aerosols are collected on a filter in a Faraday cage, assuming each particle carries one electron.

### Size Distribution

There are a number of mature instruments to measure size distribution; however, only microscopy provides the physical or geometric size, but is quite laborious. The other methods provide either the optical or aerodynamic size. Optical size is provided by optical particle counters, among the first instruments to provide size distribution, which consist of a light source, dark field scattering chamber, and photodetector. Visible wavelengths were initially used, thus optical particle counters. Particle size is determined from the intensity of scattered radiation using Mie theory. To limit the influence of Mie resonances for particles near the wavelength of light, instruments use either a white light source or a large solid angle for detection of scattered light. Both approaches smooth the counter response function and limit the sensitivity to particle index of refraction. Sensitivity is determined by particle size for small particles and by particle concentration for large particles. Scattered radiation from small particles approaches Rayleigh scattering from molecules and therefore the detection limit. Particles greater than a few micrometers are rare, thus concentration uncertainties are large; however, the signal from one particle is well above instrumental noise. An alternate ensemble approach illuminates a sample with a laser and measures the scattering pattern, which has variations dependent upon average particle size and size distribution. The fluctuations arise from constructive and destructive interference of the scattering from individual particles as they move due to Brownian motion. This technique, known as photo correlation spectroscopy, measures the mean diffusion coefficient of the particles, and hence their mean size and a rough size distribution. The technique is sensitive to nanometer sizes. To achieve sufficient aerosol concentrations, samples are often captured in a liquid, producing a colloidal suspension. If particle concentrations are high enough, such as in flames or smokes, the technique can be used directly on aerosol samples as opposed to hydrosol samples.

Aerodynamic size is measured in several ways. Differential mobility analyzers or electrostatic aerosol spectrometers consist of an aerosol charging region, a drift tube with an applied electric field, and an outlet to a particle sensor. Charging regions usually contain sources of low energy electrons or alpha particles and produce bipolar equilibrium charge distributions which are a function of size. The particles then pass to a large diameter annular opening at the beginning of the drift tube. Particles with the appropriate charge polarity are attracted across a region of filtered air to a central rod held at a specific voltage. The particle drift velocity is inversely proportional to aerodynamic size. Only particles with the appropriate charge and aerodynamic drag to arrive at a small open annulus near the central rod will exit, providing a population of uniformly sized particles. The aerosol detector is usually a CN counter, but could be a filter and Faraday cage. Scanning the center rod across a range of voltages provides a differential size distribution if the size-dependent charge distribution is known, which also accounts for multiply charged particles. If the exit annulus is replaced by a large opening, all charged particles too large for collection on the central rod will exit, providing a cumulative size distribution measurement. This approach was used by instruments called electrostatic aerosol analyzers. Final size distributions are available after an inversion. The lower size limit is constrained by inefficient charging for small particles, and the upper limit by the length of the drift tube. For supermicrometer particles, size can be measured with the aerodynamic particle sizer, which injects particles from a sample nozzle into a fast airstream. Particles are accelerated toward the airstream velocity based on their inertia and aerodynamic drag. Particles not fully accelerated prior to a velocity measurement with dual laser beams can be differentiated, based on their resistance to the airstream, which depends on both inertia and aerodynamic drag. Fully accelerated particles cannot be differentiated. Preceding both of these techniques were inertial impaction devices, using centrifugal force, cascading orifices, or counterflow for size discrimination. Centrifuges and cyclones collect the particles, which cross streamlines as the air is forced into a graduated rotation. In a cascade impactor successive nozzle diameters decrease thus increasing air velocity and capturing ever smaller particles. Nozzle diameters are designed for the sizes of interest. Counterflow, or virtual impactors only collect particles with enough inertia to resist the counterflow. In all of these techniques, the collected particles must be analyzed using standard filter and microscopy techniques.

### Mass

All aerosol mass measurements rely on aerosol capture either on filters or oscillating microbalances. All but one are gravimetric, comparing the weight of exposed and unexposed substrate. The exception uses the attenuation of a beam of β-particles (electrons) irradiating exposed and unexposed substrate. The attenuation is directly proportional to mass. There are several systems using sensitive oscillating devices such as microbalances, which provide direct, real time, mass measurements as opposed to the delayed analysis of gravimetry and β-ray attenuation. These instruments measure changes in oscillation frequency of sensitive elements as mass is accreted. The tapered element oscillating microbalance mounts a replaceable aerosol collector on the tip of the tapered element, which is oscillated by an electric field. The resonant frequency of oscillation changes as mass accumulates on the filter, through which air is flowing. Similar principles apply to piezoelectric crystal microbalances. The resonant frequencies of the metal-coated quartz crystals decrease as mass is deposited. Particles are deposited, by either electrostatic precipitation or inertial impaction onto the metal, which can become inefficient for larger solid particles due to rebound. The frequency of exposed crystals are referenced to an unexposed crystal at the same temperature, pressure, and humidity. Size differentiated mass can be obtained from these instruments by coupling them with inertial impactors or other size selecting techniques. A variation of the quartz crystal microbalance involves a technique to increase oscillation frequency from 10 to 100 MHz. This is called a surface acoustic wave and increases mass sensitivity by a factor of a thousand.

### Surface Area and Shape

Aerosol surface area is of primary interest when considering the impact of aerosol on either atmospheric chemistry or radiation.

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Most commonly, surface area is derived from other fundamental measurements such as size distribution. There are, however, several direct ways to measure surface area. These rely on a tracer colliding with and sticking to the particles. Since the collision rate depends on surface area, a measure of the number of tracers collected is a measure of the aerosol surface area, at least the 'active' surface area available for either chemical or radiative interactions. Electrical, radioactive, and photon tracers are used. For electrical tracers, a corona discharge is used for a source of unipolar ions in concentrations high enough for their collection by aerosol through Brownian motion. The charged aerosols are then captured on an impactor stage, or filter, in a Faraday cage, and the very low current (fA) measured. The current is directly proportional to the ions collected, and thus surface area. If a cascade impactor is inserted prior to particle collection, then size resolution of the surface area is available. Alternatively number distributions can be determined if the average number of charges collected per particle size is known. The epiphaniometer works similarly but uses the decay of actinium ($^{227}$Ac) to radon ($^{219}$Rn) to lead ($^{211}$Pb) to produce a source of $^{211}$Pb atoms dispersed in a chamber through which the particles flow. Downstream of the chamber with the lead atoms, the aerosol is collected on a filter below an $\alpha$ particle detector. The number of $^{211}$Pb atoms collected is measured through their $\alpha$-decay to $^{207}$Pb. The photoelectric aerosol sensor uses UV photons to irradiate aerosol samples. UV photons colliding with a particle are energetic enough to create free electrons from electrons near the particle surface. As the particles lose electrons they become charged. The free electrons ionize nearby gas molecules and move away from particles $<1$ μm. The gas ions are trapped and the charged particles collected on a filter in a Faraday cage from which the very low current is measured.

Solid particle shape is another of the difficulties of aerosol measurement. Shape affects surface area and therefore chemistry, radiational interactions, and aerodynamic drag, and thus any measurement or process depending on these properties. Shape is often accounted for by adding an adjustable shape factor used to reconcile disparate measurements of other properties. One direct measurement is through microscopy, which is useful to present the challenges which shape can provide. The depolarization of polarized light sources from backscattersondes is another option for particles >about 1 μm to indicate the extent of nonsphericity of the particles.

## Optical Properties

The optical properties of aerosol form a significant part of several of the instruments already discussed; however, aerosol scattering, absorption, and their sum, extinction, are also measured directly with ensemble instruments. Scattering is measured with a nephelometer, which consists of a monochromatic light source, sampling chamber, and photodetector. Light scattered from aerosol and gas in the sampling chamber is collected over an angular range of ~7 to ~170°. Filtered and ambient air are alternated in the sample chamber to account for variations due to air density and illumination. Some instruments include a shutter to block the forward scatter, so that both total scatter and backscatter are measured. Multiwavelength instruments are available. The backscattersonde, usually deployed on balloons or aircraft, consists of a pulsed light source and receiving optics focused on the light backscattered from 30 to 50 m from the instrument. Light sources can be xenon flash lamps, lasers, or light emitting diodes. Pulsed light sources allow comparisons of stimulated and ambient backscatter and provide instrument background. For broadband sources, detector filters provide the wavelength dependence. For monochromatic sources, several wavelengths are used. For polarized light sources, depolarization provides particle shape information. Measurements of absorption have already been discussed in the descriptions of the filter-based black carbon instruments and the photoacoustic spectrometer, while extinction measurements have been described using cavity ring-down instruments.

## Nucleative Properties

Aerosols play pivotal roles in the hydrologic balance of the atmosphere through their role as cloud condensation nuclei (CCN) and ice nuclei. Without particles we would have neither clouds nor atmospheric ice. CCN counters are similar to CN counters, with the exception that the working fluid is water and the supersaturation is much lower and more carefully controlled. Most CCN counters are based on thermal gradient diffusion chambers, which consist of parallel water saturated surfaces held at different temperatures. Since the diffusion rates of temperature and water between the surfaces differ, supersaturated regions develop in the interior. Controlling the wall temperatures controls the chamber supersaturations in the range 0.05–2.0%. Static thermal diffusion chambers operate by holding air samples drawn into the sample chamber at a single supersaturation for approximately 20 s. Scattering from the cloud of droplets is associated with a number concentration through calibration. Continuous flow thermal diffusion chambers can be operated at several supersaturations simultaneously, by maintaining several discrete temperature differences across the plates at different points in the sampling chamber. Aerosol particles are exposed to increasing supersaturations and so increasingly smaller particles will activate and grow. The droplet size at the end of the chamber, measured with a single particle optical counter, is an indication of droplet growth, which is directly related to the critical size and supersaturation of the CCN. These instruments provide a CCN supersaturation spectrum from single aerosol samples. Static diffusion chambers must adjust plate temperatures between samples to provide a supersaturation spectrum.

Because of their highly active role in precipitation, ice nuclei are even more interesting than CCN, are even harder to measure, and are much more rare. While CCN may constitute 0.1 of the ambient aerosol number concentration, ice nuclei constitute usually $<10^{-4}$ of the ambient aerosol population. There are only a few ice nuclei counters available. They all work on the same principle, mixing the aerosol into a water supersaturated environment, cooling the resulting cloud droplets, which now contain the aerosol, and counting the droplets which freeze. Differences occur due to chamber geometry and orientation, and ice particle detection methods ranging from manual to automatic. The first automated instrument detected ice acoustically as the relatively large ice particles exited a small opening. More recent instruments use optical particle counters. All the instruments primarily measure particles, which act as

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condensation freezing nuclei. Instruments to measure deposition or contact ice nuclei are not available.

### Nucleated Particles

Completing the contribution of particle measurements to our understanding of the hydrologic cycle are instruments to measure cloud droplets and ice particles. These instruments are optical and use either forward Mie scattering for cloud droplets, or geometric optics to create shadowgraphs of the particles, for ice. The sampling volumes must be adjusted for the different size ranges of interest and thus several instruments are required to cover the complete spectrum. These optical instruments have completely replaced earlier approaches, relying on impaction on films and microscopy. Because of the large particles involved they suffer from edge effects, out of focus images, and false images (*see* **Clouds and Fog:** Measurement Techniques *In Situ*).

*See also:* **Aerosols:** Aerosol Physics and Chemistry, Aerosol–Cloud Interactions and Their Radiative Forcing; Climatology of Tropospheric Aerosols; Dust; Observations and Measurements; Role in Radiative Transfer; Soot. **Arctic and Antarctic:** Arctic Haze. **Chemistry of the Atmosphere:** Observations for Chemistry (Remote Sensing): Lidar; Volcanoes: Composition of Emissions. **Clouds and Fog:** Cloud Microphysics; Measurement Techniques *In Situ*. **Optics, Atmospheric:** Optical Remote Sensing Instruments. **Radiation Transfer in the Atmosphere:** Scattering. **Satellites and Satellite Remote Sensing:** Aerosol Measurements. **Tropospheric Chemistry and Composition:** Aerosols/Particles.

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