Physico-Chemical Properties and Measurement of Ambient Particles

Petros Koutrakis and Constantinos Sioutas

Introduction

Atmospheric aerosols are complex mixtures of particles directly emitted into the atmosphere and particles that are formed during gas-to-particle conversion processes. The sources of atmospheric particles are both natural and anthropogenic. Particle size is the most important parameter in describing particle behavior and the origin, chemical and composition, removal, and residence time in the atmosphere are all related to the particle size. This chapter discusses the origin and the main characteristics of atmospheric aerosols. Particle formation and removal processes are presented. The main particle characterization methods, including direct-reading and integrated sampling instruments, are discussed. A presentation of the most common analytical methods to determine particle chemical composition is also included.

Ambient aerosols are defined as suspensions of relatively stable solid or liquid particles in the surrounding air. Generally, the term refers to the particulate matter, although the “strict” definition includes both suspended matter and the surrounding air. There are several ways to classify aerosols. The major distinction is that between primary and secondary aerosols. Primary aerosols consist of particles directly emitted into the atmosphere, whereas secondary aerosols consist of particles that are products of gas-to-particle conversion processes. Aerosols are also classified according to their sources into natural and anthropogenic aerosols. Table 2.1 shows the principal sources of natural and anthropogenic aerosols. The physical and chemical characteristics of aerosols are strongly dependent on the type of their formation mechanisms and sources as shown in Figure 2.1. On a small scale, the dynamics of primary aerosols are
Particles in Our Air: Concentrations and Health Effects


influenced by Brownian diffusion and coagulation, and on a large scale by atmospheric mixing processes. Aerosol properties are subjected to continuous changes through a number of chemical and physical processes. For example, natural sodium chloride (NaCl) particles react with anthropogenic sulfuric acid (H₂SO₄) to form Na₂SO₄ particles.

The different mechanisms of formation also influence the size distribution of ambient aerosols (Whitby 1980). Ambient particles range from 0.01 to 100 μm in diameter. The particle size range from 0.01 to 0.1 μm is known as the “ultrafine mode,” or “Aitken nuclei mode.” These particles have relatively short residence times in the atmosphere because they are physically mobile due to their Brownian diffusive motion. They are products of homogeneous nucleation of supersaturated vapors (SO₂, NH₃, NOₓ, and combustion products).
<table>
<thead>
<tr>
<th>Source of Aerosols</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Natural</strong></td>
</tr>
<tr>
<td>1 Sea spray residue</td>
</tr>
<tr>
<td>2 Windblown mineral dust</td>
</tr>
<tr>
<td>3 Volcanic effluvia (includes both direct particle emissions and particles produced by subsequent reactions of emitted gases)</td>
</tr>
<tr>
<td>4 Biogenic materials (particles emitted directly and particles produced from condensation of volatile organic compounds emitted by plants)</td>
</tr>
<tr>
<td>5 Smoke from the burning of land biota</td>
</tr>
<tr>
<td>6 Natural gas-to-particle conversion products (e.g., sulfate generated from reduced sulfur emitted from the ocean surface, marshes, etc)</td>
</tr>
<tr>
<td><strong>Anthropogenic</strong></td>
</tr>
<tr>
<td>1 Direct anthropogenic particle emissions (e.g., soot, smoke, road dust, etc.)</td>
</tr>
<tr>
<td>2 Products of the conversion of anthropogenic gases from combustion of fossil fuels (e.g., sulfate and nitrate formed from oxidation of SO$_2$ and NO$_2$, respectively)</td>
</tr>
</tbody>
</table>

*Source: Prospero et al. 1981*

The size range 0.1 to 2.5 μm is known as the “accumulation mode” or “fine mode.” They are formed by coagulation of ultrafine mode particles and through gas-to-particle conversion processes known as heterogeneous nucleation, and by condensation of gases onto pre-existing particles in the accumulation mode. The major constituents of these particles in the industrialized countries are sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$), ammonium (NH$_4^+$), elemental (EC) and organic (OC) carbon. In addition they contain a variety of trace metals formed in combustion processes. Sulfate, nitrate, and ammonium are products of gas-to-particle conversion of sulfur dioxide (SO$_2$), nitrogen oxides (NO$_x$), and ammonia (NH$_3$). A host of viable species can also be present, such as fungi, bacteria, pollen, yeasts, and viruses. Fine particles are, in general, too small to settle out (by gravity) and too large to coagulate into larger particles, and thus they have lifetimes in the atmosphere of the order of days and can be transported over long distances.

The most important factor in removal of large particles from the lower atmosphere, or troposphere, is gravitational settling. In the particle range of approximately 1–20 μm the “speed of sedimentation,” or terminal settling, is given by Stokes’ law. Stokes described the competition between two forces acting on the particles, the resistance of the air to the particle’s motion through it, which is proportional to diameter, and the
force of gravity, which is proportional to the particle mass (or the cube of the diameter). The formula for the settling velocity \( v \) becomes:

\[
n = \frac{d^2 \rho g}{18 \eta}
\]

(2-1)

where (in cgs units):
- \( v \) = the terminal settling velocity (cm/sec)
- \( \rho \) = particle density (g/cm\(^3\))
- \( g \) = acceleration caused by gravity (981 cm/s\(^2\))
- \( d \) = particle diameter (cm); and
- \( \eta \) = kinematic viscosity of air (1.8 x 10\(^{-4}\) poise)

It should be noted that the atmospheric residence time, which is roughly proportional to the inverse of the terminal settling velocity, varies as the inverse square of particle diameter. Stokes’ law also governs the removal of particles by the electrostatic or centrifugal dust suppressors in use today. These suppressors act by increasing the acceleration of the particles above that caused by gravity. The constant \( g \) in Stokes’ equation is replaced by a larger value so that the settling velocity onto the collecting surface is greater than gravity provides. However, the settling velocity still varies as the square of the particle diameter, thus although the removal efficiency for the total mass may be impressively high (i.e., 99.5 percent), the removal efficiency for the all-important respirable particles is much lower.

Particles in the size range 2.5 to 100 \( \mu \)m are referred to as coarse particles. These particles primarily contain soil and sea salt elements, such as Si, Al, Ca, Fe, Mn, Sr, Na, and K. They are produced by mechanical processes (grinding, erosion, or resuspension by the wind). They are relatively large, settle out of the atmosphere by gravity within hours or minutes and are only found near the source depending on height of release.

Figure 2.2 (Jaenicke 1980) shows the residence time of aerosols as a function of size and location in the atmosphere. Note that the residence time increases with the altitude, and also depends on a number of factors, such as the vertical distribution of water vapor which affects reactivity and removal processes and the vertical distribution of reactive chemical species. Particle size is the most important property of aerosols because it influences the lifetime of particles in the atmosphere, thus their effects on the environment and public health. These effects will be presented in more detail in the next section.
The Importance of Studying Atmospheric Aerosols

*Environmental Impact*

Atmospheric aerosols are important in the spatial distribution of substances of environmental importance. Mineral dust from arid areas is transported through aerosols to the oceans (Junge 1979, Burcher 1983). Trace elements, such as Pb, Hg, Cu, Sn, Cd, etc, are also transported by ambient aerosols, resulting in significant concentrations of such compounds in long distances from their sources (Rhan 1981). Removal of these materials through dry or wet deposition mechanisms results in high concentrations...
in soils (Romero 1982). The chemical composition of the ocean micro-layer is also affected by atmospheric aerosols (Buat-Menard 1982).

**Particle Characterization**

Sampling of atmospheric particles is a complicated task and over the past twenty years one of the main goals of environmental scientists has been to improve instrumentation for determining the properties and concentrations of ambient particles. There are two main strategies for sampling and analysis of atmospheric particles, namely direct and integrated sampling.

**Direct-Reading Instruments**

Direct-reading instruments provide instantaneous information on the concentration and size distribution of aerosols. In these instruments, the aerosol is drawn into a "sensing" region (Swift 1989). The presence of particles gives rise to a change in some property of the sensing region, which is a function of a property of the sampled aerosol. It must be noted that these instruments provide information on particle size, as well as number and mass concentration. Traditionally, these instruments have been placed into four broad categories (First 1989): optical, electrical, resonance oscillation, and beta attenuation.

Optical counters make use of the interaction between light and particles. The theory of optical aerosol behavior and its application to particle measurement is discussed by Hodkinson (1966) and Willeke and Liu (1976). Most of the optical systems count light pulses scattered from particles that flow, one by one, through an intensely illuminated zone. Sampling flow rate is low, and the smallest detectable particle size is about 0.3 μm. The use of laser beams has made it possible to count particles as small as approximately 0.1 μm (Knollenberg and Luehr 1976), although the manufacturers recommend that concentrations higher than 100 particles per cm³ should not be exceeded.

Electrical counters are based on charging the sampled aerosols and measuring the ability of particles to traverse an electrical field. Most of these counters draw particles through a cloud of either unipolarly or bipolarly charged ions, and each of the particles acquire a quantity of charge that is simply related to its size. Subsequently, the particles are drawn into a radially symmetric electrical field where particles smaller than a certain size, which depends on the intensity of the field, are collected onto the walls of the collecting device. By changing the field voltage, the particle size distribution can be obtained (Liu and Pui 1975, Whitby 1976).
When particles are deposited on an oscillating surface, the resonant frequency is a function of the mass collected on the surface. This is the principle on which resonant oscillation aerosol mass monitors are based. Most of the particle collection surfaces have piezoelectric properties. The oscillation frequency decreases as the mass loading increases, with the change proportional to the airborne mass concentration and the rate at which air is sampled through the instrument (Lundgren et al. 1976). Another instrument in this category is the tapered element oscillating microbalance (TEOM; Patacschnik and Rupprecht 1991). Aerosol is deposited on a filter which is placed on top of a tapered glass element which oscillates naturally. The deposition of particulate mass causes a decrease in the frequency, measured continuously by the oscillation amplifier.

Mass concentration of airborne particles can also be detected by attenuating beta radiation. In such instruments, aerosols are drawn through an orifice and impact on a surface positioned between a beta source and a counter (Macias and Husar 1976). One of the main drawbacks of this method is that attenuation may not be only a function of the collected mass (for instance, the chemical composition of the collected material may be an important factor).

In addition to the limitations specified above for these direct reading instrument methods, there are performance limitations due to some or all of the following factors: humidity, gas adsorption, and particle collection efficiency.

**Integrated Samplers**

**Filters.** Collection on a filter is the simplest method for determining particle concentration and chemical composition. A number of factors, such as filter density, porosity, pH, and composition, play an important role in its performance characteristics. The choice of filters depends on the chemical species to be analyzed, as well as the type of the analytical method to be used. For example, when measuring particle mass, the filter material must be non-hygroscopic, so that the net mass change before and after sampling is not affected by the ambient humidity. Another case is for trace metal analysis by XRF or neutron activation, the filter itself must be virtually free from the metals being measured. In general, aerosol sampling filters should meet the following criteria (Lippmann 1989): the collection efficiency should be above 90% for all particle sizes; they should be able to withstand sampling, transport and analysis processes; they should present low resistance to different extraction processes so that the collected particulate matter is easily removed; they should also present
low blank concentrations. Table 2.2 (Stevens 1984) shows different types of filters widely used for ambient aerosol sampling.

The simplicity of the filter techniques is a major advantage for particle sampling, but there are still potential artifacts associated with these methods. These artifacts can result in an underestimation (negative artifact) or overestimation (positive artifact) of the concentration of particles and are due to phenomena such as the following:

- Acid gas phase compounds, such as SO₂, HNO₃, and a variety of organic compounds, can be adsorbed on filter media. The high retention of atmospheric sulfur and nitrogen oxides on filter media led to measurements of atmospheric nitrate and sulfate that were too high (Coutant 1977, Appel 1984). In laboratory studies, glass fiber filters were found to retain 8–21% of the SO₂ as sulfate on the filter at 21°C and 80% relative humidity, whereas quartz and Teflon retained 5% or less. This retention is related to the filter alkalinity with the most alkaline filters retaining the greatest amount of SO₂.

Adsorption of gas phase HNO₃ onto the filter medium gives a considerable artifact nitrate on certain types of filters, leading to an overestimation of particulate-phase nitrates. In laboratory studies, glass fiber filters retained more than 94% of the gaseous HNO₃ of the sampled air, while quartz filters tested retained from 33 to 99%. Only

<table>
<thead>
<tr>
<th>Filter and Chemical Composition</th>
<th>Density (mg/cm²)</th>
<th>pH</th>
<th>Efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon Membrane (several manufacturers) (CF₂)ₙ (2 µm pore size)</td>
<td>0.5</td>
<td>Neutral</td>
<td>99.95</td>
</tr>
<tr>
<td>Cellulose (Whatman 41) (C₆H₁₀O₅)ₙ</td>
<td>8.7</td>
<td>Neutral (reacts with HNO₃)</td>
<td>58.0 at 0.3 µm</td>
</tr>
<tr>
<td>Glass Fiber (Whatman GF/C)</td>
<td>5.16</td>
<td>Basic (pH=9)</td>
<td>99.0</td>
</tr>
<tr>
<td>Quartz (Gelman)</td>
<td>6.51</td>
<td>Neutral</td>
<td>98.5</td>
</tr>
<tr>
<td>Polycarbonate (Nuclepore) C₁₅H₁₄</td>
<td>0.8</td>
<td>Neutral</td>
<td>93.9</td>
</tr>
<tr>
<td>Cellulose Acetate/Nitrate (Millipore)</td>
<td>5.0</td>
<td>Neutral (reacts with HNO₃)</td>
<td>99.6</td>
</tr>
</tbody>
</table>

* Minimum efficiency for particle diameter > 0.035 at face velocity of 10 cm/s

Source: Stevens 1984
Teflon filters adsorbed negligible amounts of gaseous HNO₃ (Shaw et al. 1982). Even when the HNO₃ is not adsorbed to the filter material, it can react with previously collected alkaline material, particularly if the coarse alkaline particles are not separated from the fine particles.

- Adsorption of vapor-phase organic compounds on quartz filters, resulting in an overestimation of the particulate phase, has been demonstrated in several laboratory studies (McDow et al. 1990, Fitz 1987).

- Particle interactions on the filter media during and after sampling, such as reactions of fine particle (< 2.5 μm) acidic sulfates with coarse (> 2.5 μm) alkaline particles such as CaCO₃, and salts such as NaCl, or NH₄NO₃, can form neutral sulfate salts and acid gases such as CO₂, HCl, or HNO₃. Such interactions between coarse and fine particles can be minimized by removal of the coarse particles using inertial impactors (see below). On the other hand, interactions between different types of fine particles collected on the same filter can be a more challenging problem.

- Volatilization of unstable ammonium particulate salts, such as NH₄NO₃, and NH₄Cl, forms NH₃ and HNO₃, or HCl (Koutrakis et al. 1992). The produced ammonia can diffuse to the collected acid sulfate particles and neutralize them, as described in the previous paragraph. The produced acidic gases can be collected by coated filters of the filter pack that are placed downstream of the particle collection filter. Thus, the gas phase concentrations would depend on the amounts that existed in the atmosphere during sampling plus the amounts that volatilized from the collected particles, resulting in an overestimation of the concentration of acidic gases and an underestimation of acidic particles. Volatilization of material from collected particles during sampling has also been observed for a number of semi-volatile organic compounds. Schwartz et al. (1981) showed that moderately polar compounds were increasingly difficult to recover as the sampling period became progressively longer. Similar observations were made by Appel et al. (1984) for semi-volatile organic compounds.

**Conventional and Virtual Inertial Impactors.** Conventional inertial impactors have been used in several studies to determine the size distribution of ambient particles (Ahlberg et al. 1978, Wang and John 1988, Pierson et al. 1989, Koutrakis et al. 1993). In these devices particles are separated from the air sample due to their inertia. In a conventional flat plate impactor (Figure 2.3), particle-laden air passes through a nozzle
where particles are accelerated. At the nozzle exit, the air streamlines are deflected sharply, so that particles larger than a certain aerodynamic size (the impactor's cut-off size) impinge on the collection surface, whereas smaller particles escape and follow the deflected streamlines. By employing more than one stage, the aerosol sample can be fractionated in several size intervals. This system is called a cascade impactor (Figure 2.4). The collected particles can be subsequently analyzed to determine their chemical composition. The nature of the impaction substrate depends on the species and the type of chemical analysis to be performed. For instance, when sampling particulate sulfate, the collection medium used as impaction surface is typically a Teflon filter, chosen for its low background acid and sulfate concentrations. For analysis of organic particles, the collection substrate is typically aluminum foil (McMurry and Zhang 1989).

Due to the extensive theoretical work (Marple and Liu 1974, Marple and Willeke 1976) the performance of conventional inertial impactors is

**FIGURE 2.3**
Schematic Diagram of a Conventional Impactor
well understood and their characteristics can be predicted quite accurately. These impactors can typically classify particles larger than a few tenths of a micrometer in diameter, operating at atmospheric pressure and having jets fabricated by conventional machining.

To classify smaller aerosol particles, low-pressure and microorifice impactors. Low-pressure impactors resemble ordinary impactors but oper-
ate at reduced pressures (0.05 to 0.4 atmospheres). These devices take advantage of the decreased aerodynamic drag on particles that occurs when the mean free path in the air is as large or larger than that of the particle diameter (Hering et al. 1978). These impactors operate at sampling flow rates up to 30 liters/minute.

Microorifice impactors reduce the impactor's cut-off size by accelerating particles through small diameter jet orifices (Marple et al. 1991). Microorifice impactors operate at pressures closer to atmospheric (0.7 to 0.9 atmospheres), and achieve cut points on the order of 0.1 μm by employing orifices 0.004 to 0.02 mm in diameter. Operation with a low pressure drop is very important, since evaporation of volatile compounds from the separated particles can result in a severe distortion of the size distribution (Biswas et al. 1987). Water loss could cause a decrease in the particle size. On the other hand, aerodynamic cooling within the high speed jet can cause particle size to increase by condensation of water vapor.

The most important limitations of these conventional inertial impactors are the following (Biswas et al. 1987): i) particles may bounce from the collection surface upon impaction; ii) collected particles may re-entrain; iii) wall losses between the impactor stages may be considerable; and iv) very large particles may break up upon impaction, especially at high impaction velocities. The particle bounce problem has been traditionally countered by coating the impaction plates with a sticky material. However, for certain analytical techniques, carbon-containing coatings which are typically used may interfere with the measurement of organic compounds.

Virtual inertial impactors provide an alternative solution to the particle bounce and re-entrainment problems associated with conventional impactors. Virtual impactors also classify particles according to their aerodynamic size (Figure 2.5). In this device, an acceleration nozzle (jet) directs particle-laden air toward a collection probe, which is slightly larger than the jet. Particles larger than a certain size (defined as the impactor's cut point) cross the air streamlines, due to their inertia, and enter the collection probe, whereas smaller particles follow the deflected streamlines. In order for the larger particles to enter the collection probe, a fraction of the total flow is allowed to pass through the probe, referred to as the minor flow (typically 10–20% of the total flow). As a result, the concentration of the larger particles in the minor flow has increased by a factor of $Q_{\text{tot}} / Q_{\text{min}}$, where $Q_{\text{tot}}$ is the total flow entering the virtual impactor and $Q_{\text{min}}$ is the minor flow. Most virtual impactors have the intrinsic disadvantage that the minor flow contains a small fraction $(Q_{\text{min}} / Q_{\text{tot}})$ of
the fine particles, as a result of pumping the coarse particle flow through the collection probe. In addition, for the same flow rate, virtual impactors have less sharp size cut-off curves than conventional impactors. Masuda et al. (1988) has developed a virtual impactor with reduced fine particle contamination of the minor flow by confining the aerosol flow within a core using an enveloping sheath of clean air. Theoretical studies of the virtual impactors are similar to those of conventional impactors (Marple and Chien 1980). The dichotomous sampler (Loo et al. 1976) has been probably the most widely used virtual impactor. It has a cut point equal to 2.5 m and fractionates coarse from fine ambient particles.
In addition to the elimination of the particle bounce and re-entrainment problem, the virtual impactors have the advantage of keeping the collected particles airborne and, by adjusting the ratio of the minor to total flow, the concentration of coarse particles can be increased by a factor of five or more. Recently, Sioutas et al. (1994) developed virtual impactors separating fine from ultrafine ambient particles. These impactors utilize slit-shaped acceleration and collection nozzles, operate at flows as high as 1000 liters/minute, and have a cut point of 0.1 µm.

Cyclones. Cyclones are devices that, similarly to impactors, utilize particle inertia to separate particles above a given size from the air sample. A typical cyclone is shown in Figure 2.6. The air sample is drawn tangentially near the top. A double vortex is created within the cyclone body. The flow spirals down the outer portion of the chamber, reverses and spirals up the inner core to the exit of the cyclone. Particles that have acquired sufficient

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**FIGURE 2.6**

Schematic Diagram of a Cyclone

angular momentum due to their inertia, are unable to follow the ascending streamlines and impact on the cyclone walls. Then they either remain on the walls or drop by gravity to the bottom of the cyclone.

Cyclones have been used extensively for collecting dust in industrial processes. They are quite large and operate at flow rates on the order of several cubic meters per second (Hering 1989). Smaller cyclones operated at a few liters per minute have also been popular in aerosol sampling because their penetration characteristics simulate the American Conference of Governmental Industrial Hygienists (ACGIH) respirable mass criteria (Lippmann 1989). Such cyclones are typically used upstream of a filter to remove non-respirable particles, so that the material collected on the filter is representative of the dose to the deeper lung.

Cyclones have several advantages over other inertial classifiers, such as impactors. They are easy to operate, they are not subject to particle bounce, hence do not require special coating for the walls of their chamber (Hering 1989). Their main disadvantage lies in the lack of a theory that describes their performance. Unlike the case of impactors, flow in cyclones is three-dimensional, thus not easily modeled. The dependence of the cutpoint on the flow rate is typically given by an equation in the form (Chan and Lippmann 1977):

\[ D_{50} = K Q^n \]  

where \( D_{50} \) is the 50% cutpoint, \( Q \) is the flow rate, \( n \) and \( K \) are empirical constants which depend on the design and dimensions of the cyclone. Summaries of theories on the performance of cyclones are given by Chan and Lippmann (1977), and Dirgo and Leith (1985).

Flow pulsation caused by diaphragm pumps can also be a source of sampling errors in cyclones, since it affects the cutpoint. This problem is especially severe in small personal cyclones and has been shown to degrade the cyclone's cutpoint (Saltzman 1984). In addition, the surface of a cyclone can be a sink for reactive gases. Appel et al. (1988) found nitric acid losses as high as 70% on cyclones used as preselective inlets upstream a gaseous collection device (such as denuders, see next paragraph).

**Impactor/denuder/filter pack systems.** During the last decade, particle sampling systems containing diffusion denuders have been used in a variety of atmospheric monitoring studies (Durham et al. 1978, Ferm 1979, Shaw et al. 1979, Forrest et al. 1982, Braman et al. 1982, and Koutrakis et al. 1988a). In these studies, glass or metallic tubes are coated with an appropriate substance to selectively collect the different gases
while allowing other gases and particles to penetrate. Particles are subsequently collected on filter media. Using this sampling technique, particles and gases are separated during sampling, thus sampling artifacts may be minimized. An annular denuder system is shown in Figure 2.7 (Koutrakis et al. 1988).

The principle of operation for diffusion denuders is that gases diffuse to the walls much faster than particles. Consequently, it is possible to trap virtually all of a given type of pollutant gas while a negligible fraction of particles are collected on the denuder walls. Different coating materials can be used to trap different gases. Sodium carbonate (Na$_2$CO$_3$), sodium hydroxide (NaOH), and potassium hydroxide (KOH) have been extensively used as a coating substrate because they very efficiently collect acidic gases such as HNO$_3$, HCl, HNO$_2$, SO$_2$, HCOOH, and CH$_3$COOH (Forrest et al. 1982, Koutrakis et al. 1988, Koutrakis et al. 1993, Lawrence and Koutrakis 1994). Citric acid has been used to collect basic gases such as NH$_3$ (Koutrakis et al. 1993). Most of the coating substrates are first mixed with glycerol, then dissolved in water or methanol, and subsequently applied to the surfaces of the denuder. The denuders are dried immediately after coating using clean air (Koutrakis et al. 1988).

The denuder/filter pack technology has made possible a number of field and laboratory studies which have enhanced our understanding of the physical chemistry of inorganic atmospheric pollutants. Such systems are cost effective because they allow simultaneous sampling of gases and particles using the same pumping system, which can be the most expensive part of the sampling unit. Moreover, the use of a denuder is necessary to prevent reactions between gases and previously collected particles on the filter media. For example, a significant portion of particulate strong acidity can be neutralized on the Teflon filter by ambient ammonia. Therefore, a citric acid-coated denuder is used upstream from the filter to remove ammonia from the air sample. In addition, either a cyclone (Appel et al. 1988), or a plate impactor (Koutrakis et al. 1990) is placed upstream from the denuder/filter pack to remove coarse alkaline particles. These devices have cutpoints at about 2.5 $\mu$m.

Analysis of the Collected Atmospheric Aerosols

Regardless of the type of integrated sampler used for measuring atmospheric particles, the procedure for chemical analysis is generally the same. The collection media (filters, impaction plates) may be weighed to determine the mass concentration of ambient particles, and then subsequently may be analyzed to determine the chemical composition of the particles.
**Figure 2.7**
The Harvard/EPA Annular Denuder Sampler (HEADS)

- **Air out**
- **Filter pack**
  - Citric acid coated filter
  - Na$_2$CO$_3$ coated filter
  - Teflon coated filter
- **Spacer/gasket**
- **Coupler**
- **2nd denuder**
- **Spacer/gasket**
- **Coupler**
- **1st denuder**
- **Glass impactor plate**
- **Accelerator jet**
- **Inlet**
- **Air in**
Weighing is typically done before and after sampling with a sensitive microbalance under controlled humidity and temperature conditions.

As discussed previously, ambient particles consist of inorganic elements and ions, including trace metals, as well as graphitic (elemental) carbon and a variety of organic compounds. Below we present some of the most standard types of chemical analysis for determining the chemical properties of ambient particles.

**Elemental analysis**

The following are the most commonly used techniques for determining the elemental composition of ambient particles.

**X-Ray Fluorescence Analysis (XRF).** This method has been used for non-destructive elemental analysis of ambient aerosols (Stevens et al. 1978). The sample is irradiated with monochromatic X-Rays. Following excitation, each element in the sample emits characteristic X-Rays which identify the element, and the intensity is used to quantify the concentration of the measured element. Elements lighter than aluminum (Al) are difficult to detect because of their low fluorescent yields and particularly because of the strong absorption of fluorescent X-Rays by the substrate on which they are collected.

**Proton-Induced X-Ray Emission (PIXE).** This technique is a non-destructive, multi-elemental procedure in which protons excite the atoms of a sample, and the characteristic emitted X-Rays are used to identify and quantify different elements in the sample (Johansson et al. 1975). PIXE is capable of measuring smaller quantities of particulate matter, although it has the same limitations with XRF for light elements. Due to its cost, PIXE is used less frequently than XRF.

**Neutron Activation Analysis (NAA).** In this method, the sample is bombarded with neutrons, and the radioactivity induced is subsequently measured. Either beta or gamma radiation can be used, but gamma is used more often due to the discrete emission wavelengths which can be used for elemental identification. Depending on the species to be measured, irradiation may last from few seconds to four hours. Limitations of this method include the fact that elements such as sulfur (S), lead (Pb), and cadmium (Cd) cannot be determined by NAA, as well as that NAA is more expensive per sample than XRF and PIXE. NAA has the advantage of higher sensitivity compared to XRF and PIXE, a fact that makes it attractive for sampling trace elements found in extremely low concentrations.

**Atomic Absorption (AA).** This method is a standard analytical tool for trace metals. The metals are extracted into solution and subsequently
vaporized in a flame. A light beam with a wavelength matching the absorption wavelength of the metal of interest passes through the vaporized sample. The light attenuated by the sample is then measured and the amount of the metal present is determined using Beer’s law. Atomic absorption has the advantage of being able to measure elements such as cadmium (Cd), lead (Pb), zinc (Zn), and magnesium (Mg). A major drawback, however, is that it cannot be used to detect sulfur. In addition, AA is time-consuming because the collected particles need to be extracted from the filter prior to being analyzed.

**Inorganic ions**

Inorganic ions, such as sulfate (SO\(_4^{2-}\)), ammonium (NH\(_4^+\)), and nitrate (NO\(_3^-\)), are major constituents of ambient particulate matter and their concentrations are typically measured using ion chromatography. To determine the concentrations of inorganic and organic ions (sulfate, nitrate, ammonium, formate, and acetate), as well as the amount of atmospheric strong acidity (H\(^+\)), the filters and the substrates are extracted using ultra-pure water.

One aliquot of the extracted solution is analyzed by ion chromatography coupled with a conductivity detector to determine particulate anion concentrations (NO\(_3^-\), SO\(_4^{2-}\) and NH\(_4^+\)). To overcome the high conductivity of the eluant, which would overwhelm the sulfate and nitrate signals, the solution passes through a suppression column that contains a strong acid resin; the carbonate is converted to CO\(_2^+\)H\(_2\)O which has a low conductivity, while nitrate and sulfate are converted to their acids (which are highly conductive). This makes it possible to detect the inorganic ions against the suppressed eluant background (Mulik et al. 1976). A second aliquot may be tested for NH\(_4^+\) by ion chromatography, using appropriate separator and suppressor columns.

Another aliquot of the extracted filters and impactor substrates can be analyzed by a pH-meter with a semi-microelectrode to determine aerosol strong acidity, H\(^+\) (Koutrakis et al. 1988). This method uses an electrode in which a potential is developed across a porous glass tube (electrode tip) in the presence of H\(^+\). The magnitude of the potential is logarithmically related to the H\(^+\) concentration, which is the measure of the strong acidity of the collected particles.

**Carbon analysis**

Carbon is one of the most abundant constituents of ambient particles. It can be present as elemental carbon (EC), which is non-volatile, and as
organic carbon (OC), which is volatile. Quartz fiber filters are used as a collection medium because they have a low carbon content and are chemically inert. Carbon analysis is based on the sequential volatilization of organic and elemental carbon followed by oxidation of carbon to CO₂.

A typical analysis is made using a modified Dohrman DC-50 organic analyzer (Huntzicker et al. 1982). Organic carbon is measured by pyrolyzing the samples to CO₂ at 650°C in a helium atmosphere and subsequent reduction of the products to methane over a nickel/hydrogen catalyst bed (Figure 2.8). The generated methane is then measured using a flame ionization detector (FID). After the analysis of organic carbon, elemental carbon is volatilized and oxidized using a 2% oxygen, 98% helium atmosphere at 850°C, converted to methane, and measured with the FID.

Although thermal analysis is a fast and simple method to determine organic and elemental carbon, during the initial heating process elemental carbon can be formed from organic carbon, leading to significant errors. In an attempt to avoid this problem, another method is to digest

---

**FIGURE 2.8**

Schematic Diagram of One Type of Thermal Analyzer for Organic and Elemental Carbon
the sample in a strongly oxidizing solution to remove organics and measure the remaining carbon on the filter. Organic carbon is determined as the difference between the total carbon on the filter before and after digestion. However, since some elemental carbon may be removed during digestion (Cadle et al. 1983), this alternate method may not be a significant improvement over thermal analysis.

An improved EC/OC sampler, involving a parallel plate denuder followed by a filter pack, has been developed by the Electric Power Research Institute (EPRI, Palo Alto, CA), and the AeroVironment (Monrovia, CA). This sampler consists of a cyclone that removes particles larger than 2.5 μm from the sample, strips of quartz filter paper in a denuder to remove vapor phase organic carbon, and two back-to-back pre-fired quartz filters to collect particulate EC/OC. The purpose of the secondary filter is to capture particulate phase organic carbon volatilized from the primary filter during sampling. The sampling flow rate is 85 liters/minute (Fitz 1990). Samples are maintained at 0°C during pre- and post-exposure storage and shipping.

Optical methods have also been used to detect continuously graphitic carbon alone (Lin et al. 1973). Light transmitted through a filter that has collected carbonaceous particles is compared to that transmitted through a clean filter to determine the concentration of elemental carbon. The Aethalometer (Model AE-9, Magee Scientific Inc., Berkeley, CA) is an example of a device based on optical methods to determine a surrogate of elemental carbon, called “black” carbon (BC). Light is attenuated by particles collected on a pre-fired quartz filter. The light source is an incandescent bulb with an effective wavelength of 820 nm. An empirically determined factor is used to convert data from this instrument (BC concentration) to EC concentration (Hansen 1984). The performance of this instrument has been tested in field studies and it was found to agree well with independent measurements of EC concentrations (Hansen 1990).

Cooper et al. (1981) converted carbon to CO₂ and then, using a low-background proportional counter, measured the ^14C to total carbon ratio. This ratio indicates the fraction of particulate carbon produced by fossil fuel versus that by “modern” sources, such as combustion of vegetation or wood. Fossil fuels contain virtually no ^14C, while modern sources present a ^14C/total carbon approximately equal to that in the atmosphere.

**Organic compounds**

The study of organic compounds is necessary in order to identify the sources releasing mostly carbonaceous particles (for example, diesel en-
gines, cars, home heaters, etc). Because of their carcinogenic nature, polycyclic aromatic hydrocarbons (PAHs) have been studied more extensively than any other organic compound. Their sampling and analysis is a difficult chemical problem, because they are partitioned in both gas and particulate phases and their collection is susceptible to sampling artifacts. Analysis of PAHs is typically carried out with high-performance liquid chromatography or thermal separation with a mass spectrometer. The first technique separates the different PAHs, whereas the second determines their mass. Extraction of the sample with an appropriate solvent can separate the organics into acid, base, and neutral fractions, as well as polar and non-polar fractions. Each fraction can be then analyzed by gas chromatographic mass spectrometry (GC-MS) to identify and measure individual organic compounds.

Schueltzle et al. (1975), and Cronn et al. (1977) used high-resolution mass spectrometry to analyze ambient particles. Particle samples were heated to sequentially volatilize various compounds into the source region of the mass spectrometer. Both temperature at which a compound vaporizes, as well as the mass spectrum are characteristic of a particular compound and used for identification. PAHs can be good pollution source tracers. For example, pyrene, fluoranthene, phenanthrene are related to emissions from diesel engines, and coronine to gasoline (Gordon et al. 1984).

Crystals. Atmospheric studies have used X-Ray Diffraction (XRD) patterns for the analysis of various crystalline materials to identify particle sources. The greatest obstacle to applying this method to aerosols is low recovery of the particles from the collection medium. Few studies reported successful recovery of crystalline particulate matter from collection media (Brosset 1978, Biggins and Harrison 1979). In the Biggins and Harrison study the particulate matter was collected by an Anderson Impactor modified so that all particulate matter below 2.1 µm would be collected on a single stage. Sampling lasted for a week to allow collection of sufficient material. The collection medium, which was a glass fiber filter paper, was ultrasonicated into aromatic-free n-hexane for 30 minutes and subsequently filtered onto a 0.22 µm millipore cellulose ester filter. The samples were analyzed by XRD with a Philips XDC700 Guiner camera using totally monochromatized Cu radiation.

A similar study, using Teflon filters, was reported by Stevens (1984). Table 2.3 lists minerals that were measured in particle samples collected in four U.S. cities and their chemical composition.
TABLE 2.3
Minerals Commonly Present in Ambient Particles That Can Be Measured by X-ray Diffraction Methodology

<table>
<thead>
<tr>
<th>Mineral Name</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biotite</td>
<td>$\text{K}_2\text{MgFe}_3(\text{FeAl})_2\text{Si}_3\text{O}_10(\text{OH})_2$</td>
</tr>
<tr>
<td>Muscovite</td>
<td>$\text{KAl}_2(\text{AlSi}_3\text{O}_10)(\text{OH})_2$</td>
</tr>
<tr>
<td>Gypsum</td>
<td>$\text{CaSO}_4\cdot\text{2H}_2\text{O}$</td>
</tr>
<tr>
<td>Kalonite</td>
<td>$\text{(FeAl)}_4\text{Si}<em>4\text{O}</em>{10}(\text{OH})_8$</td>
</tr>
<tr>
<td>Calcite</td>
<td>$\text{CaCO}_3$</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>$0.55 [\text{NaAlSi}_3\text{O}_8] + 0.45 [\text{CaAl}_2\text{Si}_2\text{O}_8]$</td>
</tr>
<tr>
<td>Dolomite</td>
<td>$\text{CaMg(CO}_3\text{)}_2$</td>
</tr>
<tr>
<td>Hematite</td>
<td>$\text{Fe}_2\text{O}_3$</td>
</tr>
<tr>
<td>Magnetite</td>
<td>$\text{FeO.F}_2\text{O}_3$</td>
</tr>
<tr>
<td>Anglesite</td>
<td>$\text{PbSO}_4$</td>
</tr>
<tr>
<td>Mascagnite</td>
<td>$(\text{NH}_4)_2\text{SO}_4$</td>
</tr>
<tr>
<td>Thenardite</td>
<td>$\text{Na}_2\text{SO}_4$</td>
</tr>
<tr>
<td>Sodaniter</td>
<td>$\text{NaNO}_3$</td>
</tr>
</tbody>
</table>

Source: Stevens, 1984

Microorganisms

The term “microorganisms” include viruses, bacteria, fungi (e.g., yeasts and molds) and spores of the latter two groups. Spores are clusters of particles from the fruiting body of a fungus or a resistant dormant structure that some bacteria produce to survive adverse conditions (Burge and Solomon 1987). The difficulty in sampling viable microorganisms arises from the fact that they are sensitive to exposure to oxygen, to extreme temperatures, and to humidity while airborne. Thus, although methods for collecting microbial aerosols are similar to those for collecting any other type of airborne particles, the procedures for analysis are very different. Identification of microorganisms can require that collected cells or spores be allowed to multiply to observable numbers. Typically, particles can be collected on semisolid nutrient agar, which is then placed in an incubator to promote cell growth. Particles can also be collected onto filters or in a liquid and transferred to a nutrient agar for growth and possible isolation of bacteria and fungi. Also direct lifting from surfaces can be used to identify microorganisms optically with a microscope or via subsequent culturing.

The literature on sampling airborne microorganisms is quite extensive. Some excellent literature reviews were done by Burge et al. (1987) and
Chatigny et al. (1989). In general, there are two types of efficiencies that need to be considered when sampling airborne microorganisms: 1) the efficiency of the sampler (e.g., the ratio of particles retained by particles entering the sampler), and; 2) the efficiency with which the viability of the microorganism is preserved (recovery). Filters are more efficient collectors of smaller particles, but viable recovery is lower than from an impactor or an impinger. Therefore, there is not a standard sampling method, and the choice of apparatus depends on the viability of microorganism to be analyzed.

Typical liquid media for collecting viruses, bacteria, and fungi include distilled water, physiological saline, phosphate buffered saline, and peptone water. Semisolid media include tryptic soy agar, blood agar, nutrient agar, and heart infusion agar (Chatigny et al. 1989). Nutritionally rich formulas, such as tryptic soy agar for bacteria, and malt extract agar for fungi, are more effective than one that permits differentiation of the collected organisms by selectively promoting or inhibiting growth. Microorganisms can also be detected by staining cells collected on filters (Palmgren et al. 1986), or by assaying the total protein content of the sample as an indicator of biological material. DNA probes and monoclonal antibody labels are rapidly advancing techniques that are being used for microorganism detection.

Summary

Atmospheric aerosols can be generated either through natural or anthropogenic sources. They can also be classified into primary and secondary aerosols, depending on whether they are directly emitted in the atmosphere, or they are generated through gas-to-particle conversion processes. Ambient particles range from 0.01–100 µm. The particle size range from 0.01 to 0.1 µm is known as the ultrafine mode, containing most (in numbers) of the ambient particles. The accumulation, or fine mode consists of particles in the size range 0.1–2.5 µm. Particles in this size range have long residence times in the atmosphere, and can be transported over long ranges. The important chemical constituents of fine particles are sulfate, nitrate, and ammonium ion; organics; and a variety of trace metals. Finally, particles larger than 2.5 µm are known as coarse particles. They are produced by mechanical processes. They are removed from the atmosphere through gravitational settling, although some are returned to the atmosphere through resuspension by the wind.

Sampling of atmospheric particles is a complicated task. Their are two main sampling strategies, depending on the information that is sought.
Direct-reading instruments provide instantaneous information on the concentration and size distribution of aerosols. According to the principle of their operation, these instruments have been placed into four broad categories: optical, electrical, resonance oscillation, and beta attenuation. Direct-reading instruments, however, do not provide detailed information on the chemical composition of particles, which can be obtained by using integrated samplers.

Integrated sampling methods include filters, impactors (inertial or virtual), cyclones, and diffusion denuders followed by filters. The advantages and shortcomings of each of these methods have been discussed. In general, there is no optimum method, and the choice of the sampling technique depends on the type of compound to be sampled and the type of analysis to be performed. Filters are the simplest method, and can be used with non-volatile compounds. However, when sampling compounds that exist in both particle and gas phases, impactors and denuders should be preferred.

Before any chemical analysis is performed, the total collected aerosol mass may be measured. Subsequently, the elemental composition of particles can be determined. Elemental composition of particles can be determined by X-Ray diffraction, particle-induced X-Ray emission, neutron activation, and atomic absorption. Inorganic ions, such as sulfate, nitrate, and ammonium, can be determined using ion chromatography. Particle acidity is measured by determining the concentration of hydrogen ions using a pH-electrode. Organic and elemental carbon are determined using thermal methods. Volatile organic carbon vaporizes first, whereas elemental carbon is oxidized at the highest temperatures. Elemental carbon can be also measured through light attenuation techniques (aethalometry). Various crystalline materials are detected using X-Ray diffraction. Microorganisms are collected on a semisolid nutrient agar, or in liquid media, and then placed in an environment that promotes their growth prior to their counting.