Chapter 9

The nature and properties of workplace airborne contaminants

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Introduction

The science and practice of occupational hygiene is concerned with the interaction between humans and the working environment. An important facet of the working environment is the surrounding air, in which numerous hazardous materials may be present. Broadly speaking, these materials are classed as air pollutants, existing as matter (gases or aerosols) or energy (heat, sound, light and ionizing or non-ionizing radiation). This chapter is concerned with airborne pollutant matter in the form of gases, vapours and aerosols.

The physical properties of matter are important in helping to understand how pollutants (gaseous or aerosol) are generated and dispersed in the workplace air, transported to the part of the worker–environment interface where they are likely to be troublesome, and monitored and controlled. This chapter sets out to provide a basic framework of relevant physical ideas. It starts with a brief résumé of the general physical properties of matter, describing how the gaseous, liquid and solid phases are related to one another and how phase changes can take place. We then describe some important properties of the air which determine the behaviour of airborne pollutants. There follows a description of the nature and behaviour of gases, vapours and aerosols, with an emphasis on those properties important to their generation and measurement in workplace environments. We then briefly describe interactions between electromagnetic radiation and airborne pollutant matter (gases, vapours and aerosols) with emphasis on applications in monitoring methods. Examples are given throughout to illustrate how knowledge of these scientific subjects is important to occupational hygienists.

In view of the wide range of topics encompassed, the treatment throughout is necessarily of an introductory nature, and the interested reader is recommended to consult more specialized texts for in-depth coverage of specific areas. Some of these

are listed in the 'Further reading' section at the end of the chapter.

Physical properties of matter

Matter is usually acknowledged to exist in three phases: solid, liquid or gas. It consists of small particles called atoms, which in turn are made up of combinations of so-called fundamental particles of matter, namely protons, neutrons and electrons. Each particular combination of these defines an element. Under certain conditions, atoms may combine together to form larger entities known as molecules. Whether or not atoms or molecules come together to form solids, liquids or gases depends on combinations of pressure, volume and temperature. The most familiar example is water, which, over the ranges of familiar terrestrial conditions, can exist as solid ice, liquid water or gaseous water vapour.

In the solid state, atoms are located in fixed positions, which, for many stable materials, are arranged in regular and periodic patterns constituting the familiar stable crystallographic lattice structure. So-called amorphous (non-ordered) materials (e.g. glasses) are not strictly stable, and in time – sometimes a very long time – become crystalline. The atoms of a solid material are held together in this ordered way by inter-atomic forces, electrostatic in nature, which may be likened to a system of invisible springs by which each is connected to its neighbours. When we speak of atoms occupying fixed positions in the crystal lattice of a solid material, it should be understood that we are referring to their mean positions. In fact, at any temperature above absolute zero, 0 kelvin (K), the atoms are in oscillatory motion about their mean locations and, as in any spring–mass system in motion, energy is continually being exchanged between the kinetic form (associated with velocity) and the potential form (associated with displacement). Averaged overall, energy is shared equally between the two energy forms.

If extra internal energy is given to a lump of solid matter in the form of heat, then the atoms perform greater excursions about their mean locations. If enough energy is supplied, the solid melts and enters the liquid phase. At that point, bonds may be broken and remade, and individual atoms can move around in the lattice, changing places with one another. The state of the material has now become 'fluid'. It is of particular interest to occupational hygienists to consider what happens near the surface of a liquid. Atoms there are connected by their invisible 'springs' only with other atoms in the general direction of the body of the liquid; so, unlike atoms in the body of the liquid, they experience a net inwards-seeking force. This accounts for the well-known phenomenon of surface tension. However, there is a statistical probability that a given atom located instantaneously near the surface of the liquid may escape from the surface as a free entity and enter the gaseous vapour phase. Thus, we have the phenomenon of evaporation. Conversely, atoms of molecules in the vapour phase may enter the liquid through the surface, and so contribute to condensation. The magnitude and direction of the net flux of molecules across the surface are controlled by complex thermodynamic considerations.

If enough energy is supplied to a liquid, then a temperature is eventually reached at which all the inter-atomic bonds can be broken permanently. All the atoms or molecules now become free to move at random, and the liquid becomes a gas in which all of the internal energy exists as kinetic energy.

The preceding scenario for the transition from the liquid to the gaseous or vapour phase applies in principle to all substances. For example, under extreme thermodynamic conditions (e.g. very low temperature), even a gas such as helium can become a liquid. In relation to occupational hygiene, however, it is the convention to refer to gases as substances, which, under workplace conditions, are always found in the free molecular phase (e.g. air). On the other hand, vapours are regarded as the free molecular phase of some other substances (e.g. organic solvents), which can, in the workplace, also be found in the liquid state.

Basic properties of gases and vapours

Occupational hygiene is concerned with the transport of pollutants of various kinds in the vicinity of

human subjects, both through and by the workplace atmospheric air. In general, vapours are produced in the workplace as a consequence of volatile liquid evaporation. Most solvents, cleaning liquids and oil-based products are highly volatile and they have an increased potential to become airborne vapour at room temperature. Gases that are non-condensable at room temperature can be released in the environment as a result of various industrial processes or from chemical reactions of solid or liquid chemicals.

Air is a mixture of gases, the main constituents being nitrogen (about 78% by volume) and oxygen (21%), with a variety of other trace gases (amounting to about 1% in total), including argon, carbon dioxide and water vapour. It is a colourless, odourless gas with a density of 1.29 kg m^{-3} at standard temperature of 293 K and pressure of 1.01×10^5 Pa sea at level (STP).

In the widest sense, 'air pollution' defines the presence in the atmospheric air of entities of matter or energy, naturally occurring or synthetic, which have the potential to cause harm. In the context of occupational hygiene, this relates to the health and well-being of employees.

The universal unit of the concentration of any pollutant is its mass per unit volume of the atmosphere itself (e.g. micrograms of pollutant per cubic metre of air, or mg m^{-3}). However, for gases and vapours it is also common to talk in terms of the partial volume occupied [e.g. parts per million (ppm) or parts per billion (ppb)]. For gases and vapours, the relationship between forms of expression is given (for STP conditions) by:

$$(\text{mg m}^{-3}) = \frac{(\text{ppm}) \times \text{MW}}{24.5\ (\text{L mol}^{-1})} \qquad (9.1)$$

where MW is the molecular weight (mass of gas or vapour in g mol^{-1}) of the material in question. Take, for example, the common gaseous air pollutant, sulphur dioxide. At a mass concentration of 0.3 mg m^{-3}, an exposed person would soon become aware of its presence. From Equation 9.1, this is equivalent to a partial volume of about 10^{-7} (or 0.1 ppm).

For aerosols, concentrations are usually expressed in terms of the mass per unit volume of air (e.g. mg m^{-3}). However, depending on the measurement method used, aerosols may also be expressed in terms of the surface area of particulate per unit volume air (e.g. as might be obtained using a light-scattering instrument) or the number of particles per unit volume of air (e.g. as might be obtained for asbestos fibres using an optical microscope).

Some of the above principles can be applied to materials, which, although normally existing in the liquid phase, can also appear as vapours in air. This is a situation commonly encountered by occupational hygienists, as not all such materials are harmless.

Vapour pressure

Vapour pressure (VP) represents the pressure that would be exerted by vapour molecules in equilibrium with the same material in liquid form inside a closed container. For a material starting out as 100% liquid in such a closed system, some of the molecules will evaporate into the vapour phase. For some materials, the attractive molecular forces between liquid molecules are relatively weak, so that the pressure exerted by that liquid in the closed container would be relatively high, as a high proportion of the material will be present in the vapour phase. Conversely, for materials with stronger intermolecular forces, relatively fewer molecules will be present in the vapour phase – so the vapour pressure will be correspondingly lower. Thus, it follows that materials with high vapour pressures are more likely to evaporate into the air than those with relatively lower vapour pressure. For example, hydrazine (N_2H_4, a colourless liquid) has a vapour pressure at STP (VP_{STP}) of 10 mmHg, whereas hexane ($CH_3(CH_2)_4CH_3$, another colourless liquid) has a vapour pressure of 124 mmHg. Thus, the magnitude of vapour exposure is likely to be greater for hexane than for hydrazine.

This discussion leads to a concept useful to occupational hygienists – the vapour–hazard ratio (VHR). For a given material, this is defined as:

$$\text{VHR} = \frac{\text{SC}}{\text{OEL}} \tag{9.2}$$

where OEL is the relevant occupational exposure limit for the material in question, established on the basis of the material's toxic properties for humans (in parts per million by volume, ppm) and where SC is the saturation concentration (also in ppm) given by:

$$\text{SC} = \frac{\text{VP}_{\text{STP}} \times 10^6}{\text{BP}} \tag{9.3}$$

in which barometric pressure (BP) is 760 mmHg.

A liquid's ambient saturation concentration reflects the magnitude of its vapour pressure compared with the vapour pressure of the air above it. When a pool of liquid is evaporating within an enclosed space, the amount of evaporated vapour within that space eventually will stabilize at an equilibrium level called *ambient saturation concentration*. If a chemical has a high ambient saturation concentration, it has a strong ability to displace air, and the concentration of the chemical's vapour in the air will be high. This property changes with temperature such that a liquid at higher temperature will have a higher ambient saturation concentration.

Applying the above to the examples of hydrazine and hexane, we obtain the following

- hydrazine: SC = 13 158 ppm and OEL = 1 ppm → VHR = 13 158
- hexane: SC = 163 158 ppm and OEL = 500 ppm → VHR = 326

from which we see that hydrazine is potentially much more hazardous to health, despite its lower vapour pressure and, hence, lower magnitude of exposure.

In some cases it is also important to consider the extent to which a material, when it is airborne, can exist as a vapour or an aerosol. To quantify this, SC – as defined above in Equation 9.3 – is first converted into a mass concentration (mg m^{-3}). This is then compared with the OEL (also expressed in mg m^{-3}). Thus, we have the following possible scenarios:

1 if SC/OEL < 1, the airborne material will appear mostly as aerosol;

2 if 1 < SC/OEL < 100, the airborne material will contain some aerosol;

3 if SC/OEL > 100, the airborne material will appear as vapour.

For example, mercury has an OEL listed as 0.05 mg m^{-3}, under the assumption that the material is present as vapour and that there is no aerosol exposure. Mercury has a vapour pressure of 1.8×10^{-3} mmHg, leading to SC = 19.6 mg m^{-3}. In turn, this leads to SC/OEL → 19.6/0.05 = 393. Therefore, this confirms that the setting of an OEL for mercury, based on the assumption of a vapour, is correct.

Density

Another physical property of pollutant gases and vapours in air is that associated with their density. Significant differences in density in relation to that of the air itself can lead to stratification. For example, we note that the density of carbon dioxide is 1.98 kg m^{-3} (compared with 1.29 kg m^{-3} for air), and it is well known that, in still atmospheres, it tends to accumulate near the floor. Although carbon dioxide is not toxic in itself, the fact that it displaces oxygen during this stratification can present a hazard to the unwary in certain confined spaces. However, this is not a problem in most industrial settings when there is usually sufficient mixing to prevent stratification.

Humidity

Water vapour is a normal constituent of air and is innocuous. So it is not a pollutant. However, it does not form a constant atmospheric constituent as the changes between phases for water (between solid ice, liquid water and gaseous water vapour) can all occur within the range of expected atmospheric conditions, even in workplaces. Atmospheres with high humidity can affect the properties and distribution of vapour and aerosol airborne pollutants. Some vapours can, under certain conditions, chemically interact with water, resulting in more harmful compounds. For example, sulphur dioxide can interact with water to produce sulphuric acid. Aerosol size distribution

and settling velocity can also be affected by the presence of water vapour.

The physical picture presented earlier to describe how molecules of a liquid can enter the gaseous vapour phase may be enlarged to enable discussion of the important environmental question of humidity. This relates to the presence in the air of free water molecules. The mass of water vapour per unit volume of air is referred to as the absolute humidity. Its partial pressure cannot exceed the vapour pressure of water for a given temperature and atmospheric pressure. It reaches a pressure of 1 atmosphere (atm) (1.01×10^5 Pa) at the temperature at which water boils (393 K).

Air is considered to be saturated with water vapour when its partial pressure becomes equal to the vapour pressure. At lower pressures it is unsaturated, and relative humidity (RH, expressed as a percentage) is given by:

$$\text{RH} = \frac{\text{partial pressure of water vapour}}{\text{vapour pressure of water at the same temperature}} \quad (9.4)$$

For a given mass concentration of water vapour in the air, RH can be raised by lowering the temperature. Conversely, raising the temperature lowers RH. The temperature at which water vapour becomes saturated is known as the *dew point*. Below this, nucleation and condensation may take place, hence the appearance in the air of water droplets visible as mist or fog.

The ideal gas laws

A gas or vapour can be completely characterized by the volume it occupies, its pressure and temperature. If N molecules are trapped in a box of volume V, the collision with the box walls will create a net force exerting a pressure p on the walls.

The temperature, T, of a gas is the result of intermolecular collision and depends on the velocity of colliding molecules. The behaviour of both vapours and gases in the workplace can be described in most cases by the ideal gas law expressed by:

$$pV = nRT \quad (9.5)$$

At sufficiently low pressure (as in the case of workplace atmosphere) the product of pressure p and volume V is proportional to the amount of gas (described as the number of kilomoles, n), the absolute temperature of the gas T, and a constant R. Experiment shows that at low enough density and pressure R has the same value for all gases, namely:

$$R = 8.314\,\text{J/kmol K} \quad (9.6)$$

R is called the *universal gas constant*. Equation 9.5 represents the equation of state for a gas or vapour – it is impossible to force a gas into a state of pressure, volume, temperature and amount that does not satisfy this expression.

Of particular interest for the occupational hygienist are the expressions derived from this law concerning the response to pressure and temperature. At constant temperature, the volume of a gas is proportional to the inverse of its pressure ($V \sim 1/p$). On the other hand, both the volume and the pressure are proportional to the temperature ($V \sim T$ with p held constant; $p \sim T$ with V held constant). These relationships are important for determining the properties of gases and vapours under various environmental or process conditions.

Because the properties of gases and vapours are listed in most cases at standard conditions of temperature and pressure, STP, it is often necessary to apply the equation of state to determine the properties of the pollutant under the real working conditions. For example, if an analytical method requires the sampling of a volume of 24 l of air at STP, to calculate the volume of air needed to be sampled at 30°C (303 K) and 1.0×10^5 Pa the following conversion needs to be applied.

$$V_{\text{new}} = V_{\text{STP}} \frac{p_{\text{STP}}}{p} \times \frac{T}{T_{\text{STP}}}$$
$$V_{\text{new}} = 24 \frac{1.01 \times 10^5}{1.0 \times 10^5} \times \frac{303}{293} \quad (9.7)$$

Under these conditions, 25 l should be sampled.

Partial pressure

The working environment is rarely composed of a single gas or vapour. In many processes, a pollutant gas or vapour is introduced into a container or room containing an initial gas or vapour.

To determine the total pressure exerted on the container or room, Dalton's law of *partial pressure* is applied. This law states that the pressure exerted by a mixture of gases behaving ideally is the sum of the pressure exerted by the individual gases occupying the same volume alone. To determine the total pressure exerted on a 10-l (10^{-2} m^3) container from two gases (e.g. 1 mol of nitrogen and 3 mol of hydrogen), the partial pressure of each component can be determined from the ideal gas law: $p_i = n_i\,(RT/V)$. The calculations give a partial pressure of 2.47×10^5 Pa (2.44 atm) for nitrogen and 7.42×10^5 Pa (7.32 atm) for hydrogen. According to Dalton's law, the total pressure will be the sum of the two partial pressures: $p_{\text{tot}} = (2.47 + 7.42) \times 10^5\,\text{Pa} = 9.89 \times 10^5\,\text{Pa}$ (9.76 atm).

Another way of expressing Dalton's partial pressure law is by using the *mole fraction*. If we have a mixture of gases A and B in the amount of n_A and n_B, then the fraction $x_A = n_A/n$ represents the mole fraction of component A present in the mixture. The sum of the total mole fractions in a mixture is unity, and the partial pressure law for the two gases can be expressed as:

$$p = p_A + p_B = \frac{(n_A + n_B)RT}{V} = \frac{(x_A + x_B)nRT}{V} \tag{9.8}$$

Transport properties of gases and vapours – diffusion

Transport processes occur in gases, liquids and solids and are not confined to mass transfer. Electrical charge, energy (heat) and momentum can be transported from one region of a system to another. In the case of gases and vapours, the transport of mass will allow the molecules to 'flow' from one region to another until equilibrium is reached. It is important to mention here that the main mass transport process for gases and vapours (diffusion) can be viewed as a passive process. The flow of gas or vapour molecules inside a container or process room, for example, will occur without any outside intervention until equilibrium is reached. Through ventilation the gas and vapour molecules can also be transferred from one region to another of the system, but in this case the pressure drop needed for the flow is mechanically created.

The mass transfer of a gas or vapour as a result of the random motion of its molecules when a concentration gradient is present is called diffusion. Diffusion is a general term referring either to a single gas or vapour that seeks to attain concentration equilibrium or to mixtures for which the equilibrium consists of uniform composition. For example, if a gas is confined to a container that is open to a low-pressure region through a small hole, the gas will flow through the hole until the pressures are equal on both sides. This process is called *effusion,* and in this case the concentration gradient is created by the differences in pressures on either side of the hole. In stricter terms, *diffusion* is the penetration of the molecules of one gas or vapour through the molecules of another until the composition is uniform throughout. In the practice of occupational hygiene, when a volatile liquid evaporates in air, the concentration in a room tends to become uniform because of the diffusion. Obviously, this process will allow for the contaminant to be diluted, creating a lower concentration throughout the room. On the other hand, as in ventilation, the contaminant will be transported to regions of the room far away from the contaminant source. In this way, people can suffer the effect of the contaminant without being aware of its immediate presence.

Graham's law states that the rate of diffusion of a gas is inversely proportional to the square root of its molecular weight. In the case of a gas A that diffuses through a gas B, Graham's law can be expressed as:

$$\frac{R_A}{R_B} = \frac{\sqrt{m_B}}{\sqrt{m_A}} \tag{9.9}$$

where R_A and R_B are the rates of diffusion of gases A and B and m_A and m_B are the molecular weights.

An important application of diffusion in occupational hygiene is the principle of passive, or diffusive, sampling of gases and vapours. The passive sampling is based on Fick's first law of diffusion:

$$J = -D\frac{dC}{dx} \tag{9.10}$$

This law states that the amount of gas or vapour passing per unit time through the unit area perpendicular to the direction of diffusion (the entity defined in this way is called flux) is proportional to the concentration gradient, dC/dx, and the diffusion coefficient, $D(cm^2\ s^{-1})$. The negative sign in this expression is due to the fact that a positive mass flow is determined by a decrease in concentration. If the geometrical parameters (surface area, length of diffusion path) of a sampler are known then the mass of gas or vapour transported through diffusion and adsorbed by a sorbent material inside the sampler is proportional to the ambient concentration of the pollutant.

Adsorption

Adsorption has been defined as the enrichment of one or more components in an interfacial layer. Although the adsorption of liquid molecules on to solid surfaces is possible, the most relevant process for occupational hygiene is the adsorption of gases and vapours onto solid, porous materials. There are two basic types of adsorption. In *chemisorption* or chemical adsorption the molecules bind to the surface as a result of the formation of a chemical – usually covalent – bond. The energy of attachment is strong and the molecules are transformed and lose their identity.

Physical adsorption occurs as the result of van der Waals interactions between the surface and the adsorbed molecules. As a result of this long-range, weak interaction, molecules are attached to the solid surface. However, the energy of this interaction is insufficient to lead to bond breaking, and thus in physical adsorption the adsorbed molecules retain their identity, although they might be stretched or bent at the proximity of the surface. Both of these processes are exothermic, but the amount of heat released in chemisorption is usually much higher than the heat released in physical adsorption, owing to the strength of the interaction.

Adsorption of gases and vapours on porous surfaces has two main applications in occupational hygiene:

1 Respirators use adsorbing materials inside chemical cartridges to prevent various organic vapours and gases entering the respiratory tract.

2 One method of sampling for gases and vapours is by drawing contaminated air through a sampling tube filled with gas/vapour-adsorbing material, and afterwards analysing the content of the adsorbent.

Both of these applications use a variety of adsorbents, but the material used most widely is activated carbon. Zeolites (an artificial adsorbent), silica, alumina or titanium oxides, as well as catalyst-impregnated activated carbon are also used, depending on the properties of the adsorbed gas or vapour.

'Activated carbon or charcoal' usually means a porous form of carbon produced by the carbonization of some naturally occurring material such as wood, peat or nut shells. The activation process takes place in two stages: carbonization followed by the removal of hydrocarbon tarry products from the interstices formed during carbonization. The final goal is to obtain a material composed of carbon crystallites with a complex pore structure increasing the surface area of the adsorbent. The internal surface of the product obtained through this process ranges from 400 to 1600 $m^2\ g^{-1}$.

The adsorption isotherm represents the central concept for characterizing adsorbents with respect to different gases and vapours. The adsorbed volume of a gas or vapour per unit mass of solid adsorbent, at a constant temperature, is a function of ambient concentration. This relationship is termed the *adsorption isotherm*, and is a measure of how an adsorbent reaches its capacity. A number of theoretical models have been developed to predict the adsorption isotherm and thus the adsorption capacity of certain adsorbents when challenged by various concentrations of gases and vapours. However, no single model can predict the adsorption behaviour of all adsorbent vapour/gas pairs.

The concept of adsorption capacity is of great importance for occupational hygiene practice. When the adsorption capacity is exceeded, the contaminant is no longer retained inside the adsorbent material and breakthrough occurs. In the case of chemical cartridges after breakthrough, toxic gases and vapours can penetrate into the respiratory system of the wearer, with possible health consequences. When breakthrough of

sampling tubes is reached, sampled gases or vapour will be lost and the obtained concentration will differ from the ambient concentration.

When a respiratory protection programme is implemented, a cartridge exchange schedule is set in place, based on the chemical usage, the type of cartridge (capacity of the activated carbon), activity and environmental conditions. Intense physical activity increases the respiration rate and therefore the service life of the cartridge will be diminished. The performance of the cartridge will also be affected by the presence of water vapours or another vapour or gas in significant amounts. Because adsorption is a surface process, if the adsorption sites are occupied by water vapours or other vapours or gases the capacity of the cartridge for a given contaminant will be significantly diminished.

Basic properties of aerosols

'Aerosol' is a scientific term that applies to any disperse system of liquid or solid particles suspended in a gas – usually air. It applies to a very wide range of particulate systems encountered terrestrially. Aerosols occur widely in workplace environments, arising from industrial processes and workplace activity, and so are of considerable interest to occupational hygienists. They take many different forms. A summary classification of a range of typical aerosols is given in Fig. 9.1. It contains not only examples of the workplace aerosols with which this book is primarily concerned, but also, for the sake of comparison, some naturally occurring and synthetic aerosols found in the outdoor atmospheric environment. Aerosols of interest to occupational hygienists include:

- *Dust*. An aerosol consisting of solid particles made airborne by the mechanical disintegration of bulk solid material (e.g. during cutting, crushing, grinding, abrasion, transportation), with sizes ranging from as low as 1 to over 100 μm.
- *Spray*. An aerosol of relatively large liquid droplets produced by mechanical disruption of bulk liquid material, with sizes ranging from 10 to 100 μm or more.

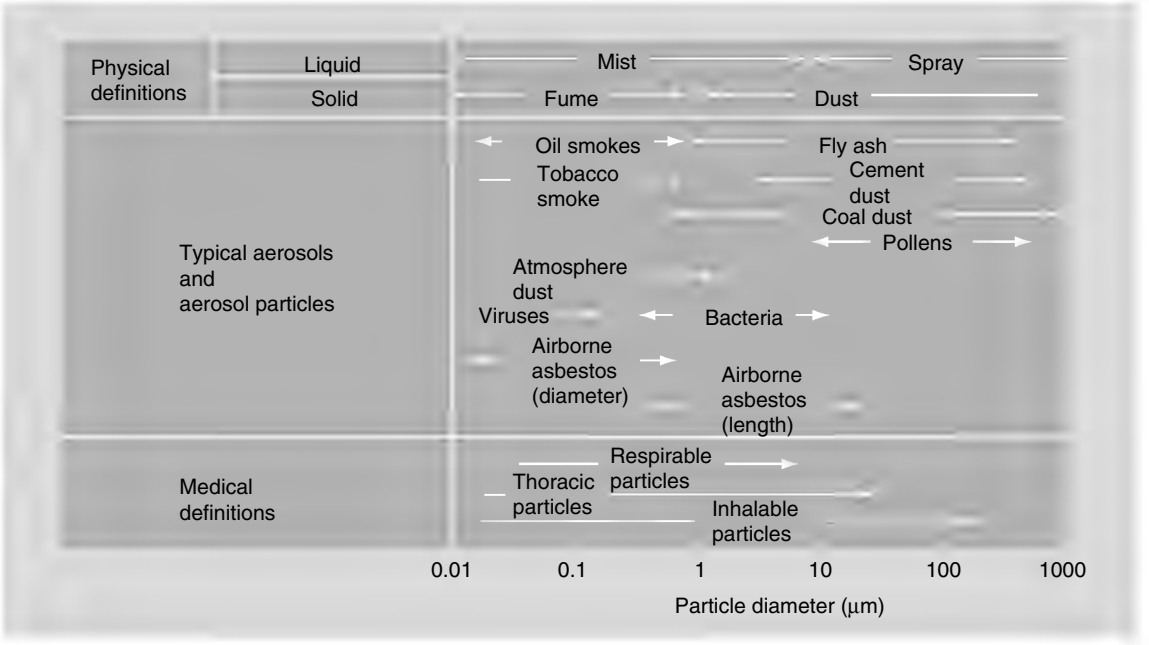

Figure 9.1 Classification of typical aerosols ('medical' definitions refer to particle size fractions where exposure to the various parts of the human respiratory tract is possible).

• *Mist*. An aerosol of finer liquid droplets produced during condensation or atomization, with sizes ranging from 0.01 to 10 μm.
• *Fume*. An aerosol consisting of small solid particles produced by the condensation of vapours or gaseous combustion products. Usually, such particles are aggregates of very small primary particles, with the individual units having dimensions of a few nanometers. Aggregates range from 0.1 to 1 μm.
• *Smoke*. An aerosol of solid or liquid particles resulting from incomplete combustion, again usually in the form of aggregates of very small (nm-sized) primary particles. The aggregates themselves have extremely complex shapes, frequently in the forms of networks or chains, having overall dimensions ranging from 0.01 to 1 μm.
• *Bioaerosol*. An aerosol of solid or liquid particles consisting of, or containing, biologically viable organisms. Viruses are generally very small, ranging from 0.01 to 0.5 μm. Bacteria are larger than viruses, ranging from 0.5 to 30 μm. Pollens are generally larger than bacteria, ranging from 10 to greater than 100 μm.

Aerosol generation in workplaces

The majority of industrial processes generate aerosols in one form or another, usually as a side-effect of the process itself and by a wide variety of physical and chemical means. These may include:
• mechanical generation of dry aerosols (e.g. during mineral extraction, smelting and refining of metals, textiles manufacture, bulk chemical production and handling, woodworking);
• mechanical generation of liquid droplet aerosols (e.g. during paint spraying, crop spraying);
• formation by molecular processes (e.g. during combustion, chemical reactions, condensation).

The evolution of aerosols

It cannot be assumed that an aerosol, once it has been dispersed, will necessarily remain in equilibrium and so retain the properties with which it began. Depending on the material in question, the initial generation process and the concentration of the aerosol, and other conditions in the surrounding air, a number of possibilities exist for evolutionary changes. These include:
• growth by coagulation, agglomeration and coalescence (by the contact of particles with and attachment to one another), in which the number concentration of particles decreases but the mass concentration stays the same;
• disintegration (when a system of particles combined together to form a single particle is subjected to external forces such that the adhesive and cohesive bonds that hold its individual elements together are broken), in which the number concentration increases but the mass concentration stays the same;
• condensation (when particles are formed and grow by the condensation of molecules out of the vapour phase), in which the mass concentration increases;
• evaporation (where particles are decreased in size – or even disappear – by the transfer of molecules from the liquid to the vapour), in which the mass concentration decreases.

These last two phenomena extend the earlier discussion about atmospheric water and other vapours to aerosols. From detailed consideration of the physics of phase transitions from liquid to vapour – and vice versa – it may be shown that, in a system of droplets of a wide range of sizes, larger droplets can grow at the expense of smaller ones.

Particle shape

Particle shape can have a significant bearing on effects relevant to occupational hygiene, for example on the way in which particles behave in the air, and how they behave after they have been deposited in the respiratory tract. Particle shape falls into a number of categories, some of which are shown schematically in Fig. 9.2. These include:
• spherical particles (e.g. liquid mists, fogs and sprays and some dry aerosols such as glassy spheres condensing out of some high-temperature processes);
• regular or isometric, non-spherical, angular particles which have no preferred dimension or whose aspect ratio cannot be said to be substantially different from unity (e.g. most dusts, including coal dust);

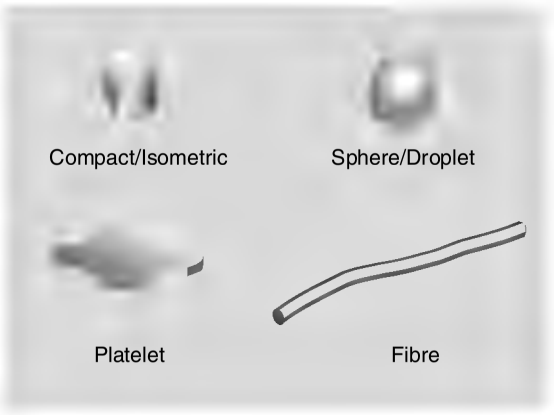

Figure 9.2 Examples of some particle shapes found in occupational hygiene.

- platelet particles (e.g. some dusts, such as mica);
- fibrous or acicular particles which are long, thin, needle-shaped particles (e.g. asbestos and man-made mineral fibre dusts);
- fractal particles, complex aggregates of much finer primary particles (e.g. fumes and smokes).

Particle size

Particle size is a property that is extremely important in virtually all aspects of aerosol behaviour. But it is a property whose definition is not always as simple as might at first appear, and can be somewhat elusive. Indices of particle size include:

- true geometric diameter (d) for a particle that is perfectly spherical;
- 'effective' geometric diameter (d') for a non-spherical particle, based on representative widths; for example, dividing a two-dimensional image of the particle into equal areas (Martin's diameter) or contained within a pair of parallel tangents to the particle perimeter (Feret's diameter);
- equivalent projected area diameter (d_p) is the diameter of a sphere that, in two dimensions, projects the same area as the particle in question;
- equivalent surface area diameter (d_A) is the diameter of a sphere that has the same surface area;
- equivalent volume diameter (d_v) is the diameter of a sphere that has the same volume;
- aerodynamic diameter (d_{ae}) is the diameter of a sphere of water (density 10^3 kg m^{-3}) that has the same falling speed in air as the particle in question (see below).

Of these, perhaps the most important in the occupational hygiene context is the last one – particle aerodynamic diameter – as this governs the airborne behaviour of most particles under most conditions, and so is relevant to the inhalation of particles by humans, deposition in the respiratory tract, sampling and air cleaning.

For some particles, none of the above definitions of particle size is truly appropriate, and further considerations need to be invoked. This is the case for fibres for which both diameter and length need to be defined. Complex aggregates such as those formed during combustion (e.g. smokes) also pose special problems. As already mentioned, these are made up of large numbers of very small primary particles and the degree of complexity is such as to render difficult the definition of size in relation to any of the measurable geometrical properties like those described above. So, although aerodynamic diameter can be usefully applied to describe aerodynamic behaviour, and a geometric diameter can be applied to describe aspects of visual appearance of individual particles or aerosols as a whole, these do not always properly convey the full nature of the particles. For many complex aggregated particles, therefore, the concepts of fractal geometry can provide further information, leading to the concept of a fractal dimension.

Elementary particle size statistics

Only rarely in practical situations – usually under controlled laboratory conditions – do aerosols consist of particles of all one size. Such aerosols are referred to as 'monodisperse'. More generally, however, in workplaces and elsewhere, aerosols consist of populations of particles having wide ranges of sizes, and so are termed 'polydisperse'. For these, particle size within an aerosol needs to be thought of in statistical terms.

Consider an ensemble of particles whose sizes can be represented in terms of a single dimension (say, d). The fraction of the total mass of particles with dimension falling within the range d to $d + \mathrm{d}d$ may be expressed as:

$$\mathrm{d}m = m(d)\mathrm{d}d \tag{9.11}$$

where

$$\int_0^\infty m(d)\mathrm{d}d = 1 \tag{9.12}$$

in which $m(d)$ is the mass frequency distribution function. Alternatively, we have directly analogous expressions for the number frequency distribution function, say $n(d)$.

In particle size statistics it is often helpful to plot distributions in the alternative cumulative form. For example, for the distribution of particle mass this is given in terms of the mass with dimension less than d, thus:

$$C_\mathrm{m}(d) = \int_0^d m(d)\mathrm{d}d \tag{9.13}$$

where C_m is the cumulative mass distribution. The fraction of mass with dimension less than d is given by:

$$\frac{\int_0^d m(d)\mathrm{d}d}{\int_0^\infty m(d)\mathrm{d}d} \tag{9.14}$$

A typical mass distribution for a workplace aerosol is shown in Fig. 9.3, both in the frequency and cumulative forms. Note here that the cumulative distribution describes the mass (e.g. in units, mg) contained in particles below the stated dimension (where now we have replaced L with d, where d is the particle diameter). As the cumulative distribution is obtained by integrating the frequency distribution, it follows conversely that the frequency distribution derives from differentiating the cumulative distribution. Thus, it is seen that the frequency distribution represents the mass fractions of particles contained within narrow size bands [and so may be expressed, for example, in units of (mg $\mu\mathrm{m}^{-1}$)].

Figure 9.3 contains a number of important features. First, the mass median particle diameter

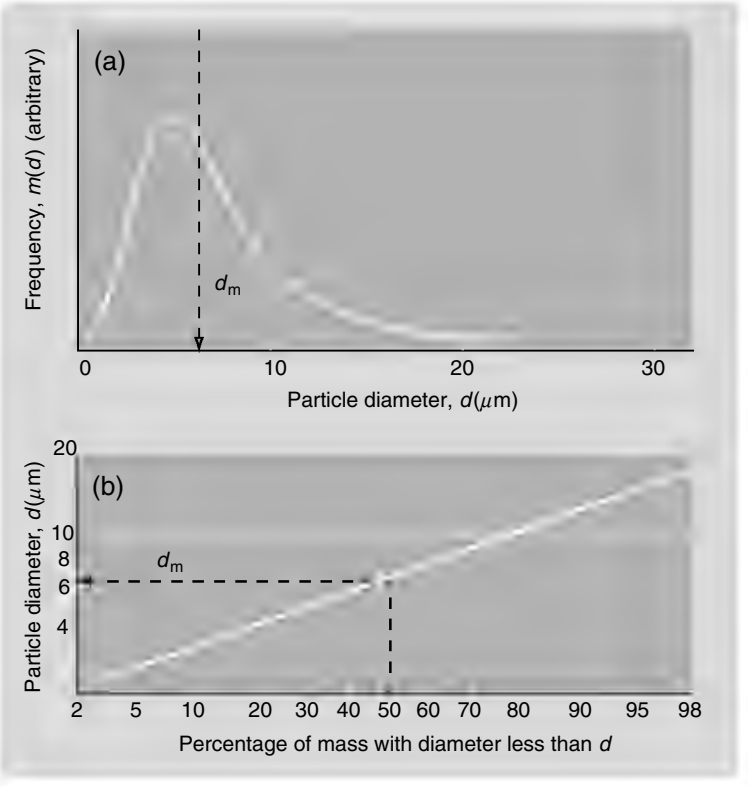

Figure 9.3 Examples of aerosol size distributions. (a) Frequency distribution; (b) cumulative distribution on log-probability axes.

(d_m), at which 50% of the mass is contained within smaller particles and 50% is contained within larger ones, can be read off directly from the cumulative plot. Second, the frequency distribution shown exhibits a strong degree of asymmetry such that the peak lies at a value of d, which is substantially smaller than d_m, and there is a long tail in the distribution that extends out to relatively large particles. This characteristic is very common in polydisperse aerosols that are found in workplace environments. Very often, the overall distribution can be represented to a fair first approximation by the log-normal mathematical function:

$$m(d) = \frac{1}{d\sqrt{2\pi}\ln\sigma_g}\exp\left[-\frac{(\ln d - \ln d_m)^2}{2(\ln\sigma_g)^2}\right] \quad (9.15)$$

where σ_g is the geometric standard deviation, reflecting the width of the distribution. This is given by:

$$\sigma_g = \frac{d_{84\%}}{d_m} = \frac{d_m}{d_{16\%}} \quad (9.16)$$

For a perfectly monodisperse aerosol, $\sigma_g = 1$. More typically for aerosols found in the workplace environment, σ_g ranges from about 2 to 3. At this point, it is useful to note that, when the cumulative distribution is plotted on log-probability axes, it appears as a straight line if the distribution is log-normal (see Fig. 9.3b). Such log-normality (or even a reasonable approximation to it) provides some additional useful aspects. In particular, it enables conversions between relationships for distributions based on particle number, mass, surface area and any other aerosol property, using a set of equations (known as the Hatch–Choate equations) that have the form:

$$q\text{MD} = \text{NMD}\exp(q\ln^2\sigma_g) \quad (9.17)$$

where NMD is the number median particle diameter and qMD is the median diameter weighted by dq. For a given particle size d, in order to get from particle number to mass we need to multiply by d^3. Therefore, it becomes obvious that $q = 3$ if we wish to use Equation 9.17 to convert distributions from number to mass.

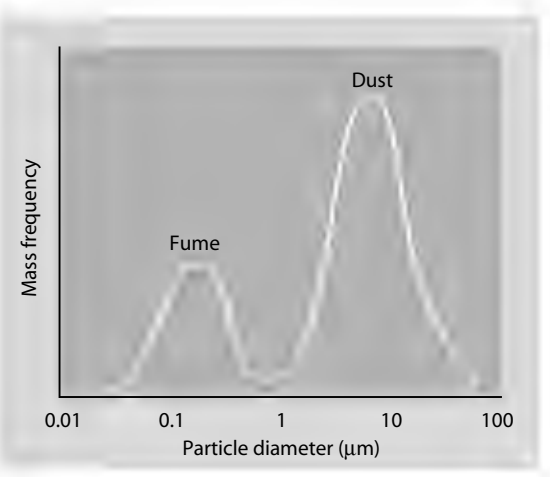

Figure 9.4 Typical bimodal aerosol frequency distribution (from an underground mining situation, showing the dust and diesel fume components).

The appearance of a log-normal particle size distribution is usually associated with a single aerosol generation process. In many workplaces, there may be more than one type of aerosol. In such cases, it is not unusual, for the aerosol as a whole, to find two or more particle size distributions superimposed. These are referred to as multimodal. A typical example is given in Fig. 9.4 for an aerosol in an underground mining situation where there is both relatively coarse dust (generated by the extraction process itself) and relatively fine diesel particulate (generated by underground transportation).

The motion of airborne particles

The physical processes governing the motion of airborne particles are highly relevant to the transport and deposition of particles in ventilation ducts, deposition onto workplace surfaces, inhalation into and deposition inside the human respiratory tract, sampling and filtration, and so on. So, an elementary appreciation of the physics of particle motion is important to occupational hygienists.

Drag force on a particle

When a particle moves relative to the air, it experiences forces associated with the resistance (by the

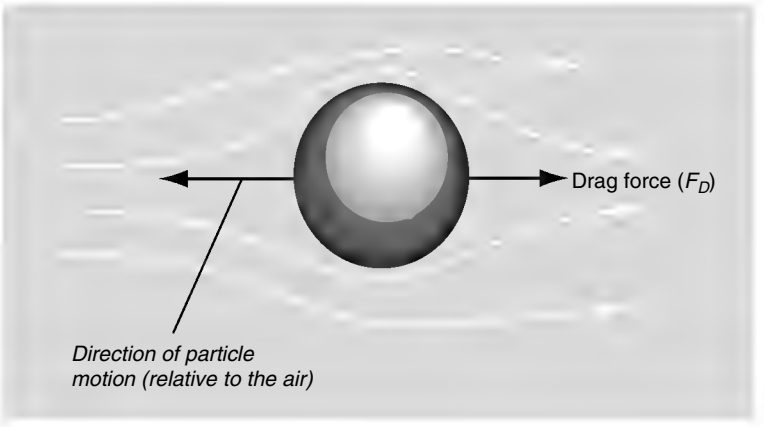

Figure 9.5 Schematic to show the drag force on an aerosol particle.

air) to its relative motion (as shown schematically in Fig. 9.5). For very slow, 'creeping' flow (at low Reynolds number) over the particle at velocity v, the drag force (F_D) is given by the well-known Stokes' law:

$$F_D = -3\pi d\eta v \tag{9.18}$$

where η is the viscosity of air. The Reynolds number for the particle, defined as:

$$Re_p = \frac{dv\rho}{\eta} \tag{9.19}$$

is very small ($Re_p < 1$) and the minus sign indicates that the drag force is acting in the direction opposing the particle's motion (ρ = density of air). Strictly, this expression should be modified by three factors. The first is the Cunningham correction factor, which derives from the fact that, in reality, the air surrounding the particle is not continuous but is made up of individual gas molecules that are in random thermal motion (so particle motion takes the form of 'slip' between collisions with individual air molecules). The second factor concerns deviations from Stokes' law at Re_p values exceeding 1. The third relates to cases (the majority in practice) when particles are non-spherical. These corrections are described in detail in the aerosol science literature. They should never be ignored. But in many occupational hygiene situations they may be quite small, so that – to a first approximation – Stokes' law may be a reasonable working assumption.

The starting point for all considerations of particle transport is the general equation of particle motion, again based on Newton's second law ('mass × acceleration = net force acting'). For the forces, the drag force describing the resistance of the fluid to the particle's motion has already been described. In addition, there may be an external force (e.g. gravity, electrical or some combination of forces), the effect of which is to generate and sustain particle motion. As long as the particle is in motion relative to the fluid, the drag force will remain finite. The proper relationship for describing the particle motion is a *vector equation*, embodying the motion of the air and the particle and the forces acting, each in all three available dimensions. It is not difficult, therefore, to envisage that the resultant set of equations that needs to be solved for particle motion in specific cases can become quite complicated. However, the important principles involved can be illustrated by reference to one simple – but nonetheless extremely important – example.

Motion under the influence of gravity

The case of a particle falling under the influence of gravity in still air is shown schematically in Fig. 9.6. The equation of motion for a spherical stokesian particle (i.e. a particle obeying Stokes' law) moving in the vertical (y) direction is given by:

$$m(dv_y/dt) = mg - 3\pi\eta dv_y) \tag{9.20}$$

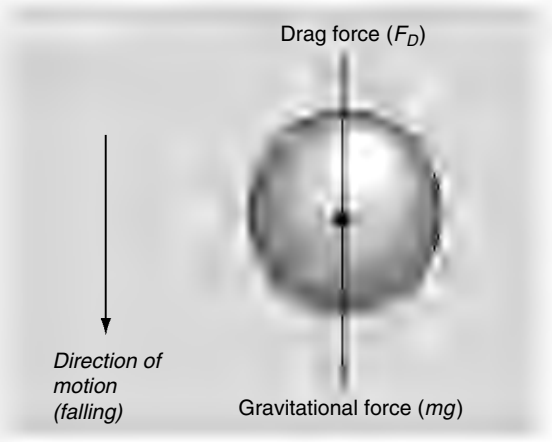

Figure 9.6 Schematic to show the forces acting on a particle of mass m moving under the influence of gravity.

where v_y is the particle's velocity in the y-direction, m is its mass and g the acceleration due to gravity. For a spherical particle, this expression may be reorganized to give:

$$dv_y/dt = (v_y/\tau) - g = 0 \tag{9.21}$$

where

$$\tau = d^2\gamma/18\eta \tag{9.22}$$

in which γ is particle density. In Equation 9.22, closer inspection reveals that τ has dimensions of time, the significance of which we shall see shortly. Equation 9.21 is a simple first-order linear differential equation of the type familiar in many areas of science and engineering. In terms of the particle velocity at time t, it has the well-known form:

$$v_y = g\tau[1 - \exp(-t/\tau)] \tag{9.23}$$

for the case when the particle starts from rest ($v_y = 0$) at time $t = 0$. This shows that particle velocity under the influence of gravity tends exponentially towards a terminal value, the sedimentation or falling speed, given by:

$$v_s = g\tau \tag{9.24}$$

Regardless of particle size (but under the broad simplifying assumption that Stokes' law applies), particle velocity reaches 1/e of its final terminal value at $\tau = t$. The quantity t is therefore referred to as the particle relaxation time. Based on the above equations, we can estimate that for a 'fine' particle with the same density as water (i.e. 103 kg m^{-3}) with $d = 1\,\mu$m, we get $v_s \sim 30$ mm s^{-1}; for $d = 5\,\mu$m we get $v_s \sim 0.8$ mm s^{-1}; and for a 'coarse' particle with $d = 20\,\mu$m we get $v_s \sim 12$ mm s^{-1} and so on. If we wished, at that stage we could estimate the appropriate value of Re for each particle size and so may inspect the extent to which the assumption of stokesian conditions is valid.

From the above, we could perform a simple 'back-of-the-envelope' calculation of the time it would take for particles of given type and size to sediment out completely in a room of given dimensions. For example, consider a cloud of monodisperse water droplets with a diameter of 20 μm uniformly dispersed into a room of a height of 3 m. Under the simplest assumptions (no air movement or other deposition mechanisms), we may estimate that all particles will have settled to the floor of the room in a time 3 m × 12 mm s^{-1}, i.e. in about 4 h.

Although the mechanism of gravitational settling is perhaps the most important in occupational hygiene, other relevant examples are those involving particle motion in electric fields or in thermal gradients. For these, the general physical approach is directly analogous to that for gravitational settling.

For two spherical particles having different diameters (d_1 and d_2) and different densities (g_1 and g_2), their falling speeds in air will be the same provided, from Equations 9.21 and 9.23, that:

$$d_1^2\gamma_1 = d_2^2\gamma_2 \tag{9.25}$$

where for simplicity, slip, Reynolds number and particle shape corrections have been neglected. Equation 9.25 leads directly to a new definition of particle size based on falling speed, namely the particle aerodynamic diameter (d_{ae}) referred to earlier. Thus, for a given near-spherical particle we have:

$$d_{ae} = d(\gamma/\gamma^*)^{1/2} \tag{9.26}$$

where d is the geometric diameter of the particle and γ^* is the density of water (103 kg m^{-3}). Note that this does not apply to particles of extreme aspect ratio, notably long and thin fibres, for which separate equations have been developed and are described in the literature.

Impaction and interception

Consider what happens in a distorted aerosol flow, as for example around a bend in a duct or about a bluff flow obstacle (Fig. 9.7). The air itself diverges to pass around the outside of the body. The flow of airborne 'inertia-less' particles would do the same. However, as described above, real particles exhibit the features of inertial behaviour, in particular the tendency to continue to travel in the direction of their original motion upstream of the body. This tendency is greater the more massive the particle, the greater its approach velocity and the more sharply the flow diverges. In the aerosol flow shown in Fig. 9.7, the result is that some particles will 'impact' on to the surface of the body. The effect is greatest for the heaviest particles approaching the body at the highest velocity. The efficiency of impaction is:

$$E = \text{Number of particles arriving by impaction/Number of particles geometrically incident on the body} \quad (9.27)$$

and is a strong function of the Stokes' number:

$$\text{St} = \frac{d^2 \gamma U}{18 \eta D} \quad (9.28)$$

where D is the body dimension and U is the velocity of the approaching airflow. If all the particles that impact onto the body in the manner indicated actually stick and so are removed from the flow, then E is also equivalent to the collection efficiency. Therefore, it is seen that impaction is important in aerosol collection in many situations, including during filtration and aerosol sampling.

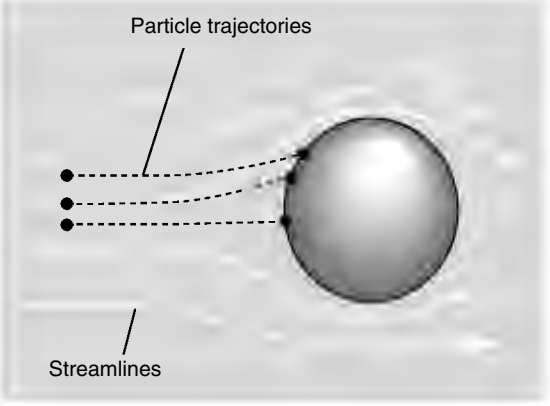

Figure 9.7 Schematic to illustrate the phenomenon of impaction.

This discussion can be extended to a particle whose trajectory, as traced by the motion of the particle's centre of gravity, passes by outside the body. If this trajectory passes close enough to the surface of the body and if the particle is geometrically large enough, it may be collected by interception, as illustrated in Fig. 9.8. Although for $d \ll D$ this effect on E is negligible, it becomes a significant influence if d becomes of the order of D, as for example it might in a filtration device made up of thin fibrous collecting elements.

Elutriation

The general term 'elutriation' is used to refer to another mode of particle deposition relevant to industrial hygiene – from a moving air stream under the influence of an externally applied force. Traditionally, the term has been used to describe the gravitational separation of particles carried along by smooth laminar flow through a narrow horizontal channel in which particles are deposited on to the floor of the channel. An extension of this idea is the gravitational elutriation that occurs during aerosol flow vertically upwards (e.g. through a vertical tube or into an inverted sampling device). The general principle also applies if some other force (e.g. electrostatic) is the main agency of deposition. The process is relevant to aerosol behaviour not only in sampling devices but also in the airways of the lung after inhalation.

Aspiration

Aspiration concerns the process by which particles are withdrawn from ambient air through an opening in an otherwise enclosed body. It is therefore relevant to aerosol sampling systems. It is also relevant to the inhalation of aerosols by humans through the nose and/or mouth during breathing.

In order to identify the nature of the process of aspiration and to enable some generalizations, Fig. 9.9 shows schematically a body of arbitrary shape placed in a moving airstream. It has a single

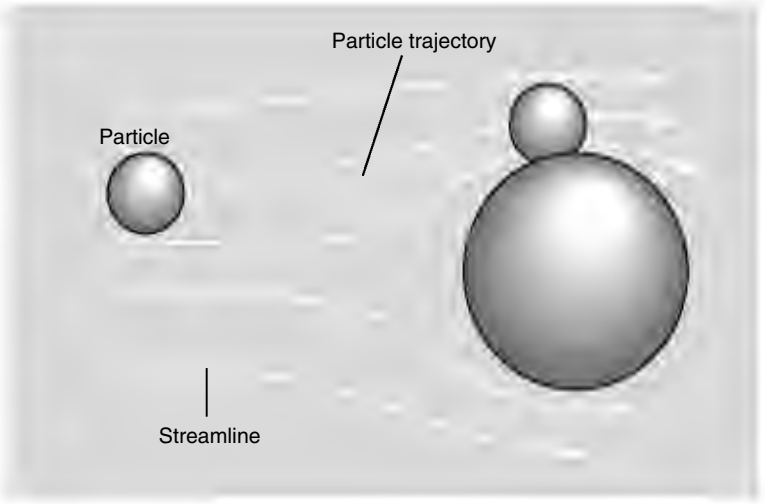

Figure 9.8 Schematic to illustrate the phenomenon of interception.

orifice located at arbitrary orientation with respect to the wind through which air is drawn at a fixed volumetric flow. There are two competing flow influences on particle transport – the external wind, which diverges to pass around the outside of the body, and the convergent flow into the orifice. The interaction between these two gives rise to the complex distorted overall flow pattern that is shown. It may be thought of as having two parts: the external divergent part and the internal convergent part.

Particles moving in this flow system respond to the changes in velocity and direction in the ways described earlier. Generally, in moving air the wind brings particles into the region of influence of the aspirating body and inertial forces provide the dominant influence on aerosol transport in that region. In fact, the system shown may be regarded as just a more complicated version of the impaction of particles on to a bluff body. This time, however, particles may be thought of as having to undergo two successive impaction processes. The first involves particles impacting on to the surface of the body and is governed by the external part of the flow. The second involves the impaction of particles in the plane of the orifice and is governed by the internal part of the flow. Having established this picture, we may begin to construct a quantitative physical model for the efficiency with which particles are aspirated from the ambient air and into the body through the orifice.

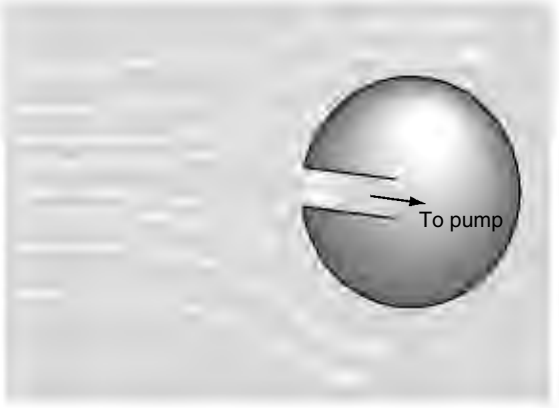

Figure 9.9 Schematic to ilustrate the concept of aspiration.

Aspiration efficiency (A) may be defined for given particle aerodynamic diameter (d_{ae}), body and orifice geometry and dimensions (D and d respectively), orientation with respect to the wind direction (q), external wind speed (u) and mean aspiration velocity (u_s) as:

$$A = \frac{\text{Concentration of particles in the air actually entering the orifice}}{\text{Concentration of particles in the undisturbed upstream air}} \quad (9.29)$$

provided that the airflow and aerosol upstream of the sampler are uniformly distributed in space. Aspiration efficiency defined in this way is the

most basic description of performance for an aerosol aspirating system (such as an aerosol sampler). Starting with Equation 9.27, and from considerations of particle impaction from one region of the flow to another, a system of equations may be developed which can, in principle, provide estimates for A. For the present purposes, it is sufficient to express some of the generalizations that arise. In the first instance:

$$A = f(\mathrm{St},\ U/U_s,\ \delta/D,\theta,B) \tag{9.30}$$

where $\mathrm{St}(= d_{ae}2^{*}U/18\eta D)$ is a characteristic Stokes' number for the aspiration system and B is an aerodynamic shape ('bluffness' or 'bluntness') factor. Second,

$$A \rightarrow (U/U_s)\cos\theta \text{ as } \mathrm{St} \rightarrow \infty \tag{9.31}$$

indicating that A levels off for large particles approaching the body at high wind speed. For very large particles and/or in environments with very little air movement, gravity may also play a role, and so an additional term – to reflect the effect of gravitational settling – may be required in Equation 9.31.

This forms the basis for understanding the performance characteristics of the simplest – and most widely researched – sampling system, the thin-walled tube. For many years, this has formed the basis of aerosol sampling in stacks and ducts under what have come to be known as *isokinetic sampling conditions*. Here, with the thin-walled sampling tube aligned axially with the flow and the sampling flow rate adjusted so that the velocity of the air entering the tube matches that in the duct (in the absence of the sampler), there is no distortion of the airstream and so particles of all sizes are aspirated with 100% efficiency (Fig. 9.10).

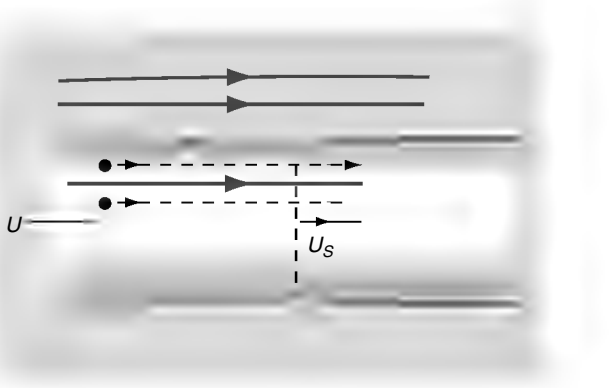

Figure 9.10 Schematic to illustrate isokinetic sampling with a thin-walled sampling tube, in which sampling velocity (U_s) is matched to the wind speed (U).

Diffusion

Particle motion has so far been assumed to be well ordered and – in theory at least – deterministic. In reality, however, even in apparently smooth airflow, aerosol particles exhibit random movement associated with their collisions with gas molecules, which themselves are in thermal motion (as described by the classical kinetic theory of gases). Such movement is independent of any convection associated with the air itself, and is known as molecular (or Brownian) diffusion. As a result of this phenomenon, there is a net migration of particles from regions of high concentration to regions of low concentration. That is, although individual particles may diffuse in either direction, a greater number end up travelling down the concentration gradient. The resultant local net flux of particles by this process is described by the well-known Fick's law of classical diffusion, which is described for the simple one-dimensional case (for the x-direction) by:

$$\text{Local net flux} = -D_B \frac{dc}{dx} \tag{9.32}$$

where c is the local concentration and D_B is the coefficient of Brownian diffusion. From classical kinetic theory for a small particle in the Stokes' regime, the latter is given by:

$$D_B = \frac{kT}{3\pi\eta d_v} \tag{9.33}$$

where T is the air temperature (in K) and k is the Boltzmann constant ($= 1.38 \times 10^{-23}$ J K^{-1}). Here, the numerator represents the thermal energy of the gas molecules that is being transferred to the particles and the denominator represents the loss of particle energy due to viscous effects. Therefore, D_B embodies the continual interchange of thermal energy between the gas molecules and particles, and vice versa. Typically, for a particle of a diameter of 1 μm in air, D_B is very small – only of the order of 10^{-11} m^2 s^{-1}.

Equation 9.32 leads directly to the general diffusion equation describing the local rate of change of concentration:

$$\frac{dc}{dt} = D_B \frac{d^2c}{dx^2} \tag{9.34}$$

whose solution for the simple one-dimensional case of N_0 particles released initially at $x = 0$ at time $t = 0$ gives the Gaussian form:

$$c(x,t) = \frac{N_0}{(2\pi D_B t)^{1/2}} \exp\left(\frac{-x^2}{4D_B t}\right) \tag{9.35}$$

for the concentration distribution along the x-direction at time t. The root mean square displacement of particles (in the one-dimensional case chosen) from their origin at time t is:

$$x' = (2D_B t)^{1/2} \tag{9.36}$$

Aerosol diffusion in a flowing gas system is referred to as 'convective diffusion', and this is perhaps the aspect that is most relevant to occupational hygiene, especially with respect to deposition. In simple terms, this may be envisaged by superimposing the possible excursion due to diffusion on the trajectories that would otherwise result in the absence of diffusion. The scaling parameter for this situation, analogous to the Stokes' number already described for inertial behaviour, is the Peclet number (Pe), given by:

$$Pe = \frac{UD}{D_B} \tag{9.37}$$

where, as before, D and U are dimensional and velocity scales respectively. The smaller Pe, the more pronounced the contribution due to diffusion.

The phenomenon of diffusion is important not only in how particles move from one point in an aerosol system to another but also how they move in relation to one another.

Interactions of airborne pollutants with electromagnetic radiation

Aerosols

Whereas most of the properties of aerosols outlined above can be directly linked – in one way or another – with health effects or environmental control, optical properties may appear to be somewhat peripheral. However, there are two aspects that are particularly relevant to occupational hygiene. The first concerns the visual appearance of a workplace aerosol. The fact that it is visible at all is usually an indication that worker exposure is high enough to demand attention. Furthermore, its visible intensity is a direct indication of the level of exposure. In addition, other qualitative features of the aerosol's appearance (e.g. colour) can provide some information about its physical nature. From such considerations, therefore, an experienced and enlightened occupational hygienist can learn a great deal from the visual appearance of a workplace aerosol. At the more quantitative level, however, the optical properties of aerosols can form the basis of sophisticated aerosol instrumentation for measuring not only aerosol concentration but also particle size characteristics.

The basic physical problem involved in the optical properties of aerosols concerns the interaction of electromagnetic radiation with individual suspended particles and with ensembles of such particles. If a particle has different dielectric properties to those of the surrounding medium, as reflected in their refractive indices, then it represents a dielectric non-homogeneity. As a result, interactions with incident light can be detected from outside. In general, the whole problem can be treated in terms of a plane electromagnetic wave incident on a particle whose geometric surface defines the boundaries of the non-homogeneity, and whose dielectric properties are described by the refractive index for the particle medium. Mathematically, it is based on Maxwell's theory of electromagnetic radiation, the solutions of which explain the well-known phenomena of reflection, diffraction, refraction and absorption. The first three of these constitute the phenomenon of light scattering; the last concerns that part of the incident energy that goes into increasing the vibrational energy of the molecules in the ordered array inside the solid particle. Such absorbed energy appears in the form of heat, raising the temperature of the particle.

There is one further process that deserves mention, namely the physical mechanism by which

radiation incident at one wavelength can be scattered at another. This occurs by virtue of so-called 'inelastic' interactions involving the absorption and re-emission of radiation energy by the individual molecules of the particle. However, such interactions do not have much direct relevance to workplace aerosols. So attention here will be focused on the simpler cases where the wavelengths of the incident and scattered radiation are the same. Such interactions are referred to as 'elastic'.

The first theory of light scattering was by Lord Rayleigh in the late 1800s, and applies to very small particles and molecules much less than the wavelength of the radiation. In effect, for visible light, this means particles with diameter of less than about 0.05 μm. Under these conditions, the particles may be treated as 'point scatterers', and the resultant mathematical treatment is relatively simple. But the most significant advance, in terms of its relevance to aerosols, came in the early 1900s when Mie extended Rayleigh's theory to larger particles.

For a beam of light energy incident on a system of many suspended particles (e.g. an aerosol), the fraction of energy that interacts in the manner indicated is either scattered or absorbed. This energy is effectively removed so that the beam itself may be regarded as having been attenuated or undergone extinction. The energy that remains in the beam is transmitted. From this picture, the interaction of light with an aerosol may be considered in one of two ways: either in terms of the extinction of the beam (or, conversely, its transmittance) or in terms of the scattered component.

The phenomenon of extinction is described by an important relation, the well-known Lambert–Beer law, which appears widely in science for describing the effects of the interactions between energy (of all types) and matter. For the passage of light through an aerosol, it is written in the form:

$$\frac{I}{I_0} = \exp(-\alpha c t) \tag{9.38}$$

where I_0 and I are the light intensities before and after passing through the aerosol respectively, c is the aerosol concentration and t is the path length through the aerosol. The important quantity is an extinction coefficient that embodies the physics of the interactions between the light and each individual particle.

Both light extinction and light scattering are relevant to occupational hygiene, in relation both to the visual appearance of aerosols and to aerosol monitoring instrumentation. Possible scenarios are summarized in Fig. 9.11.

Gases

When electromagnetic radiation passes through a gaseous medium, energy may be removed from the beam if the wavelength of the radiation is such that energy may be absorbed by the molecules of the gas. So the phenomenon of extinction again applies, and the Lambert–Beer law reappears, this time in the form:

$$\frac{I}{I_0} = \exp(-\alpha_\lambda c t) \tag{9.39}$$

where c is the concentration of the molecules with which the radiation is interacting, and I, I_0 and t are as defined above. In Equation 9.39 there is an extinction coefficient embodying the physics of the interaction between the radiation and the gas through which it passes. It refers to the absorption spectrum of the gas and is strongly dependent on the wavelength (λ). In the ultraviolet region from 0.25 to 0.40 μm, absorption takes place by electronic transitions in the gas molecules (e.g. excitation or ionization). In the visible region from 0.40 to 0.70 μm, absorption is by vibrational–rotational excitation, although this is very weak in most gases (hence their invisibility to the human eye). The only common gas for which there is significant absorption in the visible region is nitrous oxide, which occurs as a visible brown gas. In the infrared region above 0.70 μm, there are strong vibrational–rotational modes of excitation for most gases and vapours. This region is therefore particularly useful for application in detection systems for pollutant gases and, indeed, is employed widely for instruments used in the occupational hygiene setting.

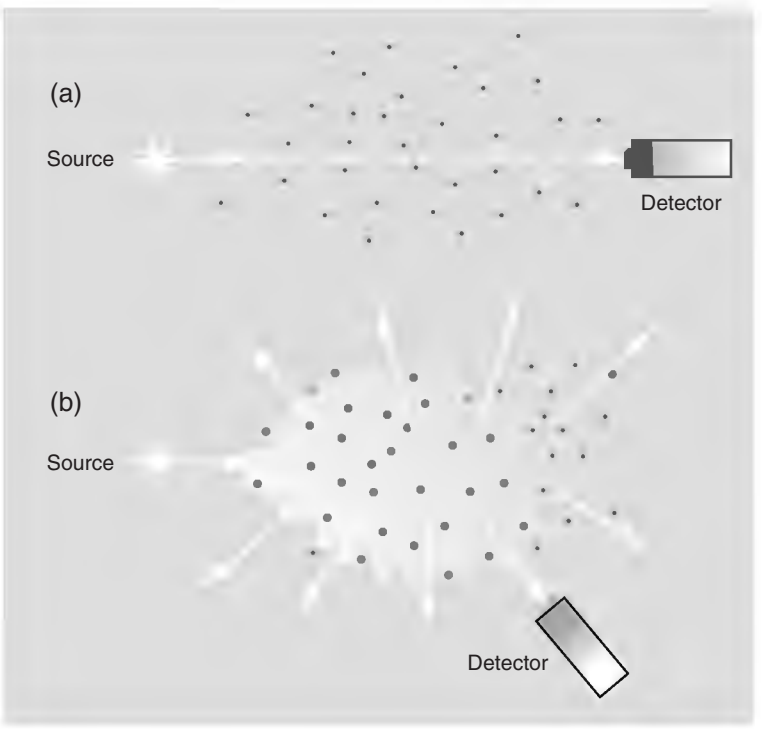

Figure 9.11 Examples of practical scenarios involving the interaction of light with particles. (a) Detection of transmitted light; (b) detection of scattered light.

Summary

This chapter has given short descriptions of various physical aspects of gases and aerosols relevant to the science and practice of occupational hygiene. These relate to the properties of airborne contaminant materials as they influence worker exposure, in particular their recognition, evaluation and control. This review underlines the point that occupational hygiene is first and foremost a scientific discipline. More in-depth background in any particular aspect described may be obtained by reference to the reading list given below.

Further reading

Cohen, B. and Hering, S. (eds) (2001). *Air Sampling Instruments for Evaluation of Atmospheric Contaminants*, 8th edn. ACGIH, Cincinnati, OH.

Hinds, W.C. (1999). *Aerosol Technology.* John Wiley & Sons, New York.

Ness, S.A. (1991). *Air Monitoring for Toxic Exposures, An Integrated Approach*. Van Nostrand, New York.

Vincent, J.H. (1995). *Aerosol Science for Industrial Hygienists*. Elsevier Science, New York.