1 Getting the basics right

Introduction: Why forensic science is a quantitative science

This is the first page of a whole book devoted to mathematical and statistical applications within forensic science. As it is the start of a journey of discovery, this is also a good point at which to look ahead and discuss why skills in quantitative methods are essential for the forensic scientist. Forensic investigation is about the examination of physical evidence related to criminal activity. In carrying out such work what are we hoping to achieve?

For a start, the identification of materials may be necessary. This is achieved by physicochemical techniques, often methods of chemical analysis using spectroscopy or chromatography, to characterize the components or impurities in a mixture such as a paint chip, a suspected drug sample or a fragment of soil. Alternatively, physical methods such as microscopy may prove invaluable in identify pollen grains, hairs or the composition of gunshot residues. The planning and execution of experiments as well as the analysis and interpretation of the data requires knowledge of units of measurement and experimental uncertainties, proficiency in basic chemical calculations and confidence in carrying out numerical calculations correctly and accurately. Quantitative analysis may require an understanding of calibration methods and the use of standards as well as the construction and interpretation of graphs using spreadsheets and other computer-based tools.

More sophisticated methods of data analysis are needed for the interpretation of toxicological measurements on drug metabolites in the body, determining time since death, reconstructing bullet trajectories or blood-spatter patterns. All of these are based on an understanding of mathematical functions including trigonometry, and a good grasp of algebraic manipulation skills.

Samples from a crime scene may need to be compared with reference materials, often from suspects or other crime scenes. Quantitative tools, based on statistical methods, are used to compare sets of experimental measurements with a view to deciding whether they are similar or distinguishable: for example, fibres, DNA profiles, drug seizures or glass fragments. A prerequisite to using these tools correctly and to fully understanding their implication is the study of basic statistics, statistical distributions and probability.

The courts ask about the significance of evidence in the context of the crime and, as an expert witness, the forensic scientist should be able to respond appropriately to such a challenge. Methods based on Bayesian statistics utilizing probabilistic arguments may facilitate both the comparison of the significance of different evidence types and the weight that should be attached to each by the court. These calculations rely on experimental databases as well as a quantitative understanding of effects such as the persistence of fibres, hair or glass fragments on clothing, which may be

successfully modelled using mathematical functions. Further, the discussion and presentation of any quantitative data within the report submitted to the court by the expert witness must be prepared with a rigour and clarity that can only come from a sound understanding of the essential mathematical and statistical methods applied within forensic science.

This first chapter is the first step forward on this journey. Here, we shall examine how numbers and measurements should be correctly represented and appropriate units displayed. Experimental uncertainties will be introduced and ways to deal with them will be discussed. Finally, the core chemical calculations required for the successful execution of a variety of chemical analytical investigations will be explored and illustrated with appropriate examples from the discipline.

1.1   Numbers, their representation and meaning

1.1.1   Representation and significance of numbers

Numbers may be expressed in three basic ways that are mathematically completely equivalent. First, we shall define and comment on each of these.

(a) *Decimal representation* is the most straightforward and suits quantities that are either a bit larger or a bit smaller than 1, e.g.

$$23.54 \text{ or } 0.00271$$

These numbers are clear and easy to understand, but

$$134000000 \text{ or } 0.000004021$$

are less so, as the magnitude or power of 10 in each is hard to assimilate quickly due to difficulty in counting long sequences of zeros.

(b) Representation in *scientific notation* (sometimes called *standard notation*) overcomes this problem by separating the magnitude as a power of ten from the significant figures expressed as a number between 1 and 10 e.g. for the examples given in (a), we get:

$$1.34 \times 10^8 \text{ or } 4.021 \times 10^{-6}$$

This is the best notation for numbers that are significantly large or small. The power of 10 (the *exponent*) tells us the *order of magnitude* of the number. For example, using the calibrated graticule on a microscope, the diameter of a human hair might be measured as $65\,\mu m$ (micrometres or microns). In scientific notation and using standard units (see Table 1.1), this becomes 6.5×10^{-5} m (metres) and so the order of magnitude is 10^{-5} m. Note that when using a calculator the 'exp' key or equivalent allows you to enter the exponent in the power of ten.

(c) An alternative that is widely used when the number represents a physical measurement, for example such as distance, speed or mass, is to attach a prefix to the appropriate unit of measurement, which directly indicates the power of ten. These are available for both large and small numbers. There are several prefixes that are commonly used, though it is worth noting that best practice is to use only those representing a power of 10 that is exactly divisible by 3. Nevertheless, because of the practical convenience of units such as the centimetre (cm) and the cubic decimetre (dm^3), these units may be used whenever needed. For example, rather than

Table 1.1. Useful prefixes representing orders of magnitude

Prefix (> 1)	Power of 10	Prefix (< 1)	Power of 10
deca (da)	10^1	*deci* (d)	10^{-1}
Hecto (h)	10^2	*centi* (c)	10^{-2}
kilo (k)	10^3	*milli* (m)	10^{-3}
Mega (M)	10^6	*micro* (μ)	10^{-6}
Giga (G)	10^9	*nano* (n)	10^{-9}
Tera (T)	10^{12}	*pico* (p)	10^{-12}

Note carefully whether the prefix is an upper or lower case letter!

write a mass as 1.34×10^{-4} kg we could write it alternatively as either 0.134 grams (g) or 134 milligrams (mg).

In summary, the example of a length of 2031.2 metres may be written in the following equivalent (represented by the symbol '≡') ways:

$$2031.2 \, \text{m} \equiv 2.0312 \times 10^3 \, \text{m} \equiv 2.0312 \, \text{km}$$

A summary of some of the available prefixes and their meanings is given in Table 1.1.

1.1.2 Choice of Representation

How do you decide which way to represent any number in your laboratory notebook or in a report? There are two reasons for thinking carefully about how the value of a particular quantity should be written down.

1. *Impact and context*.
   Ask yourself what the reader is expected to get from the number and what relevance it has to his or her understanding of the context. If the context is scientific and you are addressing a technically knowledgeable audience then numbers may be represented differently than if the context is everyday and the audience the general public.

   For example, if the order of magnitude of the number is the important feature then few significant figures may be used. If your report or document is for a non-scientific audience then perhaps it is better to avoid scientific notation. On the other hand, as it is difficult to appreciate a decimal number packed with zeros, it may be preferable to express it in prefixed units, such as mm or μm for example.
2. *Justification*.
   How many significant figures can you justify and are they all relevant in the context? If a number is the result of a pure calculation, not involving experimental data, then you may quote the number to any number of significant figures. However, is there any point in this? If the intention is to compare the calculated answer with some other value, perhaps derived from experiment or to use it to prepare reagents or set up instrumentation, then there may be no point in going beyond the precision required for these purposes. Be aware, however, that if the number is to be used in further calculations you may introduce errors later though over-ambitious rounding of numbers at early stages in the calculation.

For example, suppose we wish to cut a circle that has a circumference C of 20 cm from a sheet of paper. The calculated diameter d required for this is found, using a standard 10 digit display calculator, from the formula:

$$d = \frac{C}{\pi} = \frac{20}{\pi} = 6.366197724 \text{ cm}$$

This is the mathematically correct answer given to the limits of the calculator's capability. However, the measurement of this circle, on the paper before cutting out, is likely to be done with a ruler, at best marked with a millimetre scale. Hence, quoting this diameter to anything better than two significant figures ($d = 6.4$ cm) is pointless and displays poor scientific practice.

On the other hand, if you are undertaking calculations that include experimentally measured quantities, it is not necessary to work with more significant figures than are justified by the precision of these measurements. When making such measurements, including extra significant figures that are guesses or unreasonable estimates is not good practice as these figures are not significant. As a guiding general principle, your final answer should be quoted to a similar level of significance as the least precise numbers included in the calculation itself.

For example, say we wish to estimate the value of π, by measuring the diameter and circumference of a circle drawn on paper using a ruler, we may obtain values such as $C = 19.8$ cm and $d = 6.3$ cm. Using the calculator we calculate π as follows:

$$\pi = \frac{C}{d} = \frac{19.8}{6.3} = 3.142857143$$

Despite this output from the calculator, 10 significant figures cannot possibly be justified from this calculation. Given that the diameter is measured to two significant figures, the best we can reasonably expect from this answer is 3.1.

To understand in greater detail the justification for the quoted precision in such calculations, we have to study experimental uncertainties in more detail (Section 1.3). As a general principle however, in most experimental work it is good practice to work to four significant figures in calculations, then to round your final answer to a precision appropriate to the context in the final answer.

1.1.3   Useful definitions

In the previous section a number of important terms have been used, which need to be formally defined as their use is very important in subsequent discussions.

Significant figures: this is the number of digits in a number that actually convey any meaning. This does not include any information on the order or power of ten in the number representation, as this can be conveyed by other means. Some examples, showing how the number of significant figures is determined, are given in Table 1.2.

Truncating a number means cutting out significant digits on the right hand side of the number and not changing any of the remaining figures.

Rounding means reducing the number of significant figures to keep the result as close as possible to the original number. Rounding is always preferable to truncation. Note that when rounding a number ending in a 5 to one less significant figure we conventionally round it up by one.

Table 1.3 compares the results of both truncation and rounding applied to numbers.

Table 1.2. Examples of significant figures

Number	Number of significant figures
43.909	5: all are relevant
1.04720	6: the final zero is relevant as it implies that this digit is known; if it is not then it should be left blank
0.000203	3: as only the zero between the 2 and the 3 conveys any meaning, the others convey the order of magnitude.
3	1: obviously
3.00	3: implies the value is known to two decimal places
300	1: as the two zeros just give the order of magnitude (this last example is ambiguous as it could be interpreted as having 3 significant figures since the decimal point is implicit)

Table 1.3. Examples of rounding and truncation

Number	Truncated to			
	5 figures	4 figures	3 figures	2 figures
	4.5527	4.552	4.55	4.5
4.55272	Rounded to			
	4.5527	4.553	4.55	4.6

1.1.4 Estimation

It always pays to think intelligently when working with numbers. Nowadays, when the calculator will do all the hard work and provides an answer with more significant figures that you could ever need, it is still necessary to look at the result and ask yourself "Is that a reasonable answer?". Things can go wrong when using a calculator: a number may be entered incorrectly or misread from the display; the wrong operation may be entered so you carry out a division rather than a multiplication, and so on. Having the skill to estimate the correct answer, as well as an awareness of how errors can occur, are invaluable to the practising scientist.

In this context, *estimation* means being able to calculate the order of magnitude of an answer using a pencil and paper. The aim is not to decide whether the result given by the calculator is exactly correct but to determine whether or not it is of the expected size. This is achieved by carrying out the calculation approximately using only the powers of ten and the first significant figure in each number in the calculation. There are only two rules you need to remember for dealing with orders of magnitude:

multiplication means adding the powers of 10: $10^x \times 10^y = 10^{x+y}$

division means subtracting powers of ten: $\dfrac{10^x}{10^y} = 10^{x-y}$

Each number is rounded to one significant figure and the appropriate arithmetical calculations carried out as shown in the worked exercises.

Worked Exercises

Exercise *Estimate the results of the following calculations without using a calculator:*

(1) $\dfrac{\left(1.72 \times 10^2\right) \times \left(6.16 \times 10^5\right)}{3.88 \times 10^3} \approx \dfrac{2 \times 6}{4} \times 10^{2+5-3} = 3 \times 10^4$

(2) $\dfrac{3.1416 \times \left(2.06 \times 10^{-4}\right)^2}{7.68 \times 10^{-3}} \approx \dfrac{3 \times 2^2}{8} \times 10^{-4-4-(-3)} = 2 \times 10^{-5}$

A further estimation skill is to be able to use your experience, general scientific knowledge and ingenuity to deduce the approximate size of a physical quantity such as a length or mass, for example. Sometimes we do this by imaginary experiments; e.g., to estimate the width of a cotton thread, imagine it lying against the scale of ruler and visualize the measurement. Other approaches include making simplifying approximations of shape, for example. This skill is helpful in planning and designing experiments as well as deciding whether the values entered into you laboratory notebook are reasonable!

Worked Example

Example *In the study of shoeprints on soft ground it is necessary to estimate the pressure exerted by the individual responsible. The formula for pressure in this context is:*

$$P = \frac{Mg}{A}$$

where $g \sim 10\,ms^{-2}$, *M is the body mass and A the contact area with the surface.*

Solution To estimate P we need to make sensible estimates of M and A. Assuming an average male adult was responsible for the shoeprints, we may estimate the corresponding body weight to be around $75\,kg$ and the shape and size of each shoe to a rectangle with dimensions $10\,cm$ by $30\,cm$. This gives:

$$P = \frac{75 \times 10}{2 \times 10 \times 10^{-2} \times 30 \times 10^{-2}} = \frac{750}{0.06} = 1.25 \times 10^4 \, \mathrm{N\,m^{-2}\,(Pa)}$$

The factor of two in the denominator is to account for the weight being distributed over two shoe soles!

Self-assessment exercises and problems

1. Complete Table 1.4. For the first two columns, express your answer in standard units.

Table 1.4. Data required for self-assessment question 1

Decimal	Scientific notation	Prefixed units
0.0025 m		
	5.4×10^5 kg	
		181 µg
	3.652×10^{-2} m^3	
		1.19 cm^2

2. Round the following numbers to three significant figures:
   (a) 126.545   (b) 0.064 3573   (c) 1.6346×10^3 (d) 1.9996×10^{-2}

3. Estimate the results of the following calculations without using your calculator:

   (a) $(3.9 \times 10^2) \times (7.8 \times 10^{-3}) \times (1.2 \times 10^5)$ (b) $\dfrac{8.9912 \times (3.81 \times 10^{-4})}{9.21 \times 10^3}$

   (c) $\dfrac{(7.77 \times 10^{-2})^2 \times (2.91 \times 10^8)}{5.51 \times 10^{-3}}$ (d) $\dfrac{(1.6 \times 10^{-19})^2}{12.56 \times (8.85 \times 10^{-12}) \times (5.3 \times 10^{-10})^2}$

4. Estimate the following to one significant figure, explaining your method:
   (a) the separation of fingerprint ridges
   (b) the diameter of a human hair
   (c) the width of an ink-line on paper
   (d) the surface area of an adult body
   (e) the mass of a single blood drop from a cut finger.

1.2   Units of measurement and their conversion

1.2.1   Units of measurement

Measurements mean nothing unless the relevant units are included. Hence a sound knowledge of both accepted and less commonly used units, together with their inter-relationships, is essential to the forensic scientist. This section will examine the variety of units used for the key quantities you will encounter within the discipline. In addition to a brief discussion of each unit, a number of worked examples to illustrate some of the numerical manipulations needed for the inter-conversion of units will be included.

However, not only should units be declared in our measurements, but more importantly, all the units we use should be from a standard system where each quantity relates to other quantities in a consistent way. For example, if we measure distance in metres and time in seconds, velocity will be in metres per second; if mass is quoted in kilograms then density will be in kilograms per cubic metre. A consequence of this is that the evaluation of formulae will always produce the correct units in the answer if all quantities substituted into the formula are measured in the appropriate units from a consistent system.

Both in the UK and the rest of Europe, the *Systèm Internationale*, or SI, units based on the metre, kilogram and second, is well established and extensively used. In the US, many of the *imperial* or *British engineering* units are still actively used, in addition to those from the SI. In the imperial system, the basic units are the foot, pound and second. In some engineering contexts worldwide, units from both systems exist side by side. Occasionally, measurements are quoted using the, now defunct, CGS system, based on the centimetre, gram and second. Generally CGS quantities will only differ from those in the SI system by some order of magnitude but this system does include some archaic units which are worth knowing as you may come across them in older publications. You will also find that in some areas of forensic science such as ballistics, non-SI units predominate.

Nowadays, forensic scientists should work in the internationally accepted SI system. However, this is not always the case across the discipline, world-wide. As a result, when using non-SI data or when comparing work with those who have worked in another system it is essential to be able to move between systems correctly. The key units from SI and non-SI systems, together with their equivalencies, are given in Appendix I. Some features of these units will now be discussed.

1.2.1.1   Mass

The SI unit of mass is the kilogram (kg), though very often the gram (g) is used in practical measurement. The imperial unit is the pound weight (lb), which comprises 16 ounces (oz); $1\,lb = 453.6\,g$. Very small masses are sometimes measured in grains (440 grains per oz); for example precious metals, bullets etc. Large masses are often quoted in tonnes ($1\,tonne = 1000\,kg = 2200\,lbs$), which is almost, but not quite, the same as the imperial ton (note the spelling) ($1\,ton = 2240\,lb$).

1.2.1.2   Length

The SI unit of length is the metre, though we use the centimetre and millimetre routinely. For microscopic measurement the micrometre or micron ($1\,\mu m = 10^{-6}\,m$) is convenient, whilst for topics at atomic dimensions we use the nanometre ($1\,nm = 10^{-9}\,m$). Imperial units are still widely used in everyday life: for example, the mile, yard, foot and inch. At the microscopic level, the Ångström ($10^{-10}\,m$) is still commonly used, particularly in crystallographic contexts.

1.2.1.3   Time

The unit of time, the second (s), is common across all systems. However, in many contexts, such as measurement of speed or rates of change, the hour ($1\,h = 3600\,s$) and the minute ($1\,m = 60\,s$) are often much more convenient for practical purposes. Nevertheless, in subsequent calculations, it is almost always the case that times should be written in seconds.

1.2.1.4   Volume

Volume is based on the SI length unit of the metre. However, the cubic metre (m^3) is quite large for many purposes so often the cm^3 (commonly called the cc or cubic centimetre), or mm^3 are used. The litre ($1\,L = 1000\,cm^3$) is also a convenient volume unit, though not a standard unit. It is worth remembering that the millilitre is the same quantity as the cubic centimetre ($1\,mL = 1\,cm^3$). Rather than use the litre, it is preferable now to quote the equivalent unit of the cubic decimetre

($1\,L = 1\,dm^3$), though the former unit is still widely used in the literature. Imperial units are not, for the most part, based on a corresponding length unit so we have gallons and pints, though the cubic foot is sometimes used. Note that the UK gallon and the US gallon are different! 1 UK gallon $= 277.42\,in^3$ while 1 US gallon $= 231\,in^3$.

1.2.1.5   Density

Density is an important forensic quantity as it can be used to identify pure metals from their alloys and to match glass fragments. Density ρ is the mass per unit volume and is therefore expressed mathematically as the ratio of mass M to volume V:

$$\rho = \frac{M}{V}$$

The units of density follow the mathematics of the formula to give $kg\,m^{-3}$. Sometimes we use the relative density of a substance compared with that of water. This is also called the specific gravity (SG). Thus:

$$SG = \frac{\rho}{\rho(\text{water})}$$

Since this is a ratio of densities, SG is a pure number with no units. The density of water at $20°C$ is $998\,kg\,m^{-3}$ but is normally taken as $1000\,kg\,m^{-3}$ or $1\,g\,cm^{-3}$. Densities of liquids and solids vary from values just below that of water, such as for oils and solvents, to over $10\,000\,kg\,m^{-3}$ for heavy metals and alloys.

1.2.1.6   Concentration

This is a quantity that is often encountered in the chemical analysis of forensic materials that occur in solution – such as drugs or poisons. It is similar to density in that it can be expressed as a ratio of mass to volume. However, in this case the mass refers to the solute and the volume to the solvent or sometimes the solution itself. These are different substances and so concentration is a different concept to density. The mass is often expressed in molar terms (see Section 1.4.1) so that the concentration is given in moles per dm^3 ($mol\,dm^{-3}$), for example. Sometimes we include the mass explicitly as in $mg\,cm^{-3}$ or $\mu g\,dm^{-3}$; for example, the legal (driving) limit in the UK for blood alcohol may be stated as $0.8\,g\,dm^{-3}$. An alternative approach is to ratio the mass of the solute to that of the solvent to give a dimensionless concentration, which may be stated as parts per million (ppm) or parts per billion (ppb) by mass or alternatively by volume. These concepts will be discussed in greater detail later in section 1.4. Note the practical equivalence of the following units:

$$1\,dm^3 \equiv 1\,L$$

$$1\,cm^3 \equiv 1\,cc \equiv 1\,mL$$

$$1\,g\,cm^{-3} \equiv 1\,g\,cc^{-1} \equiv 1000\,kg\,m^{-3}$$

$$1\,mg\,cm^{-3} \equiv 1\,g\,dm^{-3}$$

1.2.1.7   Force

This is an important quantity not just on its own but more particularly as the basis for the units of pressure, work and energy. Force may be usefully defined as the product of mass and acceleration. On the Earth where the acceleration due to gravity is $9.81\,\mathrm{ms}^{-2}$, the consequent force on a mass is its weight. The Newton (N) is the SI unit of force and is equivalent to the $\mathrm{kg\,m\,s}^{-2}$. The imperial unit is the pound force (lb), with 1 lb force $= 4.45\,\mathrm{N}$. There is also the CGS unit of force called the dyne (1 dyne $= 10^{-5}\,\mathrm{N}$).

1.2.1.8   Pressure

This quantity has more units in regular use than any other! The SI unit is the $\mathrm{N\,m}^{-2}$ commonly called the Pascal (Pa). This reminds us of the definition of pressure as:

$$\mathrm{Pressure} = \frac{\mathrm{Force}}{\mathrm{Area}}$$

In the imperial system the corresponding unit is the pound per square inch or psi.

We can also measure pressure relative to the atmospheric pressure on the earth's surface, which is around $10^5\,\mathrm{Pa}$. This precise value is called 1 bar. However, a pressure of exactly $101\,325\,\mathrm{Pa}$ is termed 1 atmosphere, and so both these units may be conveniently used for pressures on the Earth's surface, but it should be noted that they are not precisely equivalent. As pressure can be measured experimentally using barometric methods, we occasionally use units such as mm Hg (1 mm Hg $=$ 1 Torr) to describe pressure. This represents the height of a column of mercury (Hg) that can be supported by this particular pressure.

1.2.1.9   Temperature

Within forensic science most temperature measurements will be encountered in degrees Celsius ($^\circ$C), where $0\,^\circ$C is set at the triple point – effectively the freezing point – of water and $100\,^\circ$C at its boiling point. However, many scientific applications use the absolute temperature or Kelvin scale, where the zero point is independent of the properties of any material but is set thermodynamically. Fortunately, the Kelvin degree is the same as the Celsius degree, only the zero of the scale has been shifted downwards, so the scales are related by:

$$T_\mathrm{K} = T_\mathrm{C} + 273.15$$

The Fahrenheit temperature scale is now extinct for most scientific purposes.

1.2.1.10   Energy

The wide range of units for energy has arisen as part of the historical development of our understanding of this important concept. The SI unit is, of course, the Joule (J), which is $1\,\mathrm{N\,m}$ in fundamental units. In describing electrical energy we may use the kilowatt-hour (kW-h), where $1\,\mathrm{kW}\text{-}\mathrm{h} = 3.6 \times 10^6\,\mathrm{J}$. For the energies typical of atomic processes, the unit of the electron-volt is used frequently; $1\,\mathrm{eV} = 1.602 \times 10^{-19}\,\mathrm{J}$. In spectroscopy you will also meet energies defined in terms of the spectroscopic wavenumber (cm^{-1}). This unit arises from the De Broglie formula, which may be used to define the relationship between energy E and wavelength λ as:

$$E = \frac{hc}{\lambda}$$

In this formula $c = 2.998 \times 10^8 \, \mathrm{ms}^{-1}$ is the speed of light and $h = 6.626 \times 10^{-34} \, \mathrm{Js}$ is Planck's Constant. This may be re-arranged to convert energy in eV to wave-number in cm^{-1}, as follows:

$$\frac{1}{\lambda} = \frac{E}{hc} = 8065 \times E \, \mathrm{cm}^{-1} \text{ where } E \text{ is in eV}$$

An alternative version of this equation may be used to convert wavelength in nm to energy in eV:

$$E = \frac{1240}{\lambda} \, \mathrm{eV} \text{ where } \lambda \text{ is in nm}$$

The *calorie* or often the *kilocalorie* may be used to describe chemical energies – for example the energies of foods. $1 \, \mathrm{cal} = 4.186 \, \mathrm{J}$ is the appropriate conversion factor. The imperial unit is the foot-pound, which is remarkably close to the joule as $1 \, \mathrm{ft\text{-}lb} = 1.356 \, \mathrm{J}$. However, we more frequently come across the *British Thermal Unit* or *BTU*, to describe large amounts of energy, such the heat emitted from burning processes, with $1 \, \mathrm{BTU} = 1055 \, \mathrm{J}$.

1.2.1.11   Power

Power is the rate of doing work or expending energy. The units of power are closely linked to those for energy, with the SI unit being the Watt where $1 \, \mathrm{W} = 1 \, \mathrm{J \, s}^{-1}$. Other units for power are linked in a similar way to those for energy. The exception is the *horsepower*, which is unique as a stand-alone unit of power.

1.2.1.12   Other quantities

Once we move away from the core mechanical units there are far fewer alternatives to the SI units in common use, so no details will be given here. Should you come across an unexpected unit there are many reliable reference texts and websites that will give the appropriate conversion factor.

1.2.2   Dimensions

The concept of dimensions is useful in determining the correct units for the result of a calculation or for checking that a formula is correctly recalled. It is based on the fact that all SI units are based on seven fundamental units, of which five are of particular relevance – the metre, kilogram, second, kelvin and mole. The remaining two – the ampere and the candela – are of less interest in forensic science. Further information on the fundamental units is given at, for example, www.npl.co.uk. Some examples of building other units from these have already been given, e.g.

$$\rho = \frac{M}{V}$$

This equation tells us that the units of density will be the units of mass divided by the units of volume to give $\mathrm{kg \, m}^{-3}$. To express this in terms of dimensions we write the mass units as M and the length units as L to give ML^{-3}.

To determine the dimensions of pressure we follow a similar approach. The units here are Pascals, which are equivalent to $N\,m^{-2}$. The Newton however is not a fundamental unit, but is equivalent to $kg\,m\,s^{-2}$. Writing the Pascal dimensionally therefore gives:

$$MLT^{-2} \times L^{-2} \equiv ML^{-1}\,T^{-2}$$

A useful application of dimensionality occurs when dimensions cancel to give a dimensionless quantity, e.g. an angle (see Section 4.1.1) or a simple ratio, such as specific gravity. Many mathematical functions that we shall meet in the following chapters act on dimensionless quantities. For example, the sine of an angle must, by definition, be a pure number. Consider an equation from blood pattern analysis such as

$$\sin\theta = \frac{W}{L}$$

where W and L are the length dimensions of an elliptical stain. This is a satisfactory form of equation as the dimensions of W and L are both length, so they cancel to make W/L a pure number.

Worked Problem

Problem   *Explain why a student, incorrectly recalling the formula for the volume of a sphere as $4\pi R^2$, should realize she has made a mistake.*

Solution   The units of volume are m^3 so the dimensions are L^3. Any formula for a volume must involve the multiplication together of three lengths in some way. Inspection of this formula shows its dimensions to be L^2, which is an area and not a volume. Note that this formula is actually that for the surface area of a sphere.

1.2.3   Conversion of units

The ability to convert non-SI units into SI units, or even to carry out conversions within the SI system such as $km\,h^{-1}$ to $m\,s^{-1}$, is a necessary competence for the forensic specialist. This is not something that many scientists find straightforward, as it involves an understanding of the principles together with some care in application. Although it is best learned by worked examples, some indications of the general method are helpful at the start.

The basic principle is to write each of the original units in terms of the new units then to multiply out these conversion factors appropriately to get a single conversion factor for the new unit. For example, to convert a density from $g\,cm^{-3}$ to $kg\,m^{-3}$, the conversion factor will be derived as follows.

$$1\,g = 10^{-3}\,kg \text{ and } 1\,cm = 0.01\,m \text{ to give a conversion factor} = \frac{10^{-3}}{(0.01)^3} = \frac{10^{-3}}{10^{-6}} = 10^3.$$

Thus $1\,g\,cm^{-3}$ is the same as $1000\,kg\,m^{-3}$. Note that we divide these two factors since density is "per unit volume". In other words, volume is expressed as a negative power in the statement of the density units.

Worked Examples

Example 1. *A car is travelling at* $70\,km\,h^{-1}$ *before being involved in a collision. Express this speed in standard units.*

Solution 1. The standard SI unit for speed is $m\,s^{-1}$. Since $1\,km = 1000\,m$ and $1\,h = 3600\,s$, we can obtain the conversion factor from:

$$\frac{1000}{3600} = 0.2778$$

Therefore the equivalent speed v in standard units is $v = 70 \times 0.2778 = 19.44\,m\,s^{-1}$. Alternatively, this calculation may be completed in a single step, as follows:

$$v = 70 \times \frac{1000}{3600} = 19.44\,m\,s^{-1}$$

Example 2. *A spherical shotgun pellet has a diameter of* 0.085 *in and there are* 450 *such pellets to the ounce. Calculate*:

(a) *the pellet diameter in mm*
(b) *the mass of one pellet in g*
(c) *the density of the pellet material in* $kg\,m^{-3}$.

The volume of a sphere is given by $4\pi r^3/3$.

Solution 2.

(a) Convert the pellet diameter to m: $0.085 \times 2.54 \times 10^{-2} = 2.16 \times 10^{-3}\,m = 2.16\,mm$.
(b) Calculate the mass of a single pellet in oz then convert to g in a single step:

$$m = \frac{1}{450} \times 28.35 = 0.0630\,g$$

(c) Calculate the volume of a pellet in m^3 (standard units), remembering to convert diameter to radius:

$$V = \frac{4}{3}\pi \left(\frac{2.16 \times 10^{-3}}{2} \right)^3 = 5.277 \times 10^{-9}\,m^3$$

Then the density in $kg\,m^{-3}$, $\rho = \dfrac{0.0630 \times 10^{-3}}{5.277 \times 10^{-9}} = 11940\,kg\,m^{-3}$.

Example 3. *Peak pressure in a rifle barrel is* $45\,000\,lb\,in^{-2}$. *Express this in (a) Pa (b) bar.*

Solution 3.

(a) Using the conversion factors of $1\,\text{lb force} = 4.45\,\text{N}$ and $1\,\text{in} = 2.54 \times 10^{-2}\,\text{m}$, we can calculate the pressure in Pa as:

$$P = 45000 \times \frac{4.45}{\left(2.54 \times 10^{-2}\right)^2} = 3.104 \times 10^8\,\text{Pa}$$

Since the pressure depends on inversely on area, which has dimensions L^2, the conversion factor for inches to metres needs to be squared in this calculation.

(b) Since $1\,\text{bar} = 10^5\,\text{Pa}$, the conversion is trivial: $P = 3.104 \times 10^3\,\text{bar}$.

Self-assessment problems

1. Pressure P is linked to the height of a mercury barometer h by the formula:

$$P = \rho g h$$

The density of mercury $\rho = 13.53\,\text{g cm}^{-3}$ and $g = 9.81\,\text{m s}^{-2}$. Calculate the height of the mercury column in metres, at a pressure of 1 atmosphere, to three significant figures.

2. A small cache of diamonds is examined by density measurement to determine whether they are genuine or simply cut glass. Their volume, measured by liquid displacement, is found to be $1.23\,\text{cm}^3$ while their mass is determined by weighing to be 48 grains. By calculating their density in g cm^{-3}, determine whether the cache is genuine. Standard densities are given as diamond, $3.52\,\text{g cm}^{-3}$, and glass, $\sim 2.5\,\text{g cm}^{-3}$.

3. A $0.315''$ calibre rifle bullet has a mass of 240 grains.
   (a) Convert its diameter and mass to SI units.
   (b) If the bullet has a kinetic energy of $2000\,\text{ft lb}$, calculate its speed in m s^{-1}.

   Note that the speed v is related to kinetic energy T by $v = \sqrt{\dfrac{2T}{m}}$.

4. The heat of combustion of gasoline is the energy released as heat through the complete burning of a kilogram of the material and has a value of $43.7\,\text{MJ kg}^{-1}$. In addition the specific gravity of gasoline is 0.751. In a fire, $5000\,\text{L}$ of gasoline are consumed. Calculate the total heat generated in
   (a) J   (b) BTU.

5. If the legal limit for alcohol in blood is $0.8\,\text{mg cm}^{-3}$, express this in
   (a) mg dm^{-3} (b) g L^{-1}.

6. In an IR spectrum, an $H-O-H$ bend occurs at $1618\,\text{cm}^{-1}$. Express the energy of this absorption in: (a) eV (b) J.

1.3   Uncertainties in measurement and how to deal with them

1.3.1   Uncertainty in measurements

All measurements are subject to *uncertainty*. This may be due to limitations in the measurement technique itself (resolution uncertainty and calibration uncertainty) and to human error of some sort (e.g. uncertainty in reading a scale). It is evidenced by making repeat measurements of the same quantity, which then show a spread of values, indicating the magnitude of the uncertainty – the *error bar*. The level of uncertainty will determine the *precision* with which the number may be recorded and the *error* that should accompany it. The precision is essentially given by the number of significant figures in the quantity under discussion, a high precision reflecting small uncertainty in the measurement. It is clearly difficult to determine the uncertainty in a single measurement but it can be estimated through careful consideration and analysis of the measurement method and process.

If the true value of the quantity is known then we can identify the *accuracy* of the measurement. This is extent to which our measurement agrees with the true value. It is important to fully appreciate the difference between precision and accuracy. This may be illustrated by comparing the measurement of mass using two different instruments – a traditional two-pan balance and a single-pan digital balance.

The former method compares the unknown mass against a set of standard masses by observation of the balance point. The precision can be no better than the smallest standard mass available, and so this is a limiting factor. The measurement is always made by judgement of the balance point against a fixed scale marker which is a reliable technique so any measurement should be close to the correct value. This method is therefore accurate but not necessarily precise. On the other hand, the digital balance will always display the value to a fixed number of significant figures and so it is a precise technique. However, if the balance is not tared at the start or has some electronic malfunction, or the pan is contaminated with residue from an earlier measurement, then the displayed mass may not be close to the correct value. This method therefore may be precise but not necessarily accurate.

If all goes well, the true value should lie within the range indicated by the measurements, noted to an appropriate precision, and the error bar may be interpreted from this data using the *method of maximum errors*. Strictly, this should be a statistical comparison, based on the probability relating the position of the true value to that of the measured value, but this is for future discussion in Section 10.1.1. For the moment we shall consider the principles of error analysis by the maximum error method. This implies that, should a measurement and its uncertainty be quoted, for example, as 3.65 ± 0.05, then the true value is expected to lie between 3.60 and 3.70.

The uncertainty in the measurement x may be expressed in two ways.

The *absolute uncertainty* is the actual magnitude of the uncertainty Δx.
The *relative uncertainty* is obtained by expressing this as a fraction or percentage of the measured value, e.g.

$$\frac{\Delta x}{x} \text{ or } \frac{\Delta x}{x} \times 100$$

Note that we use the Greek symbol Δ – upper case delta – to represent a small difference between two values of the same quantity: in this case the spread of values given by the uncertainty.

Experimental uncertainties may be classified into two categories.

1. *Random uncertainties* produce a scatter of measurements about a best value. These may arise from a variety of causes, such as poor resolution, electrical noise or other random effects, including human failings such as lack of concentration or tiredness! They cannot be eliminated from any measurement but may be reduced by improved techniques or better instrumentation. For a single measurement, the uncertainty must be estimated from analysis of the measurement instruments and process. For example, in using a four-figure balance, draughts and other disturbances may mean that the last figure in the result is not actually reliable. So, rather than quoting a result as say, 0.4512 ± 0.00005 g, which indicates that the value of the last digit is accepted, it may be more realistic to state 0.4512 ± 0.0003 g if fluctuations indicate an uncertainty of three places either way in the fourth digit. In Section 1.3.2 we shall see how the uncertainty arising from random errors may be assessed and reduced by the use of repeat measurements.

2. A *systematic uncertainty* can arise through poor calibration or some mistake in the experimental methodology. For example, using a metre stick to measure length when the zero end of the scale has been worn down so that the scale is no longer valid will now give readings that are systematically high. Incorrect zeroing (taring) of the scale of a digital balance or some other instrument are common sources of systematic error. Such effects often result in an offset or constant error across a range of values that is sometimes called *bias*. However, they can also give rise to uncertainties that increase or decrease as measurements are made across a range. In principle, systematic uncertainties may be removed through proper calibration or other improvements to the measurement procedure, though they may be difficult to discover in the first place.

1.3.2   Dealing with repeated measurements: outliers, mean value and the range method

It is often the case that an experiment may be repeated a number of times in order to obtain a set of measurements that ideally should be the same but that because of random errors form a set of numbers clustered around some mean value. Where some measurements within a set deviate significantly from the mean value compared with all the others they are called *outliers* and may be evidence of an occasional systematic error or some unexpectedly large random error (gross error) in the data. Outliers should be identified by inspection or by plotting values along a line, and then omitted from any averaging calculation. For example, from the following series of repeat measurements – 6.2, 5.9, 6.0, 6.2, 6.8, 6.1, 5.9 – the solitary result of 6.8 looks out of place as it is numerically quite separate from the clustering of the other measurements and should be disregarded. Note that there are more formal, statistically based methods for identifying outliers, which will be examined in Section 10.6. For the moment, you should be aware that a critical approach to data, including an awareness of outliers, is a vital skill for the experimental scientist.

Estimation of the random uncertainty or error bar in a quantity can be improved through such repeated measurements. Statistically, the magnitude of the uncertainty may be reduced through analysis of such a set of measurements. Where only random errors are present, the best value is given by the *average* or *mean* value $\overline{x}$ for the set of measurements, x_i:

$$\overline{x} = \frac{x_1 + x_2 + \cdots\cdots + x_n}{n} = \frac{1}{n}\sum_{i=1}^{n} x_i$$

The "capital sigma" symbol Σ is shorthand for taking the sum of a series of values x_i, where the symbol "i" provides an index for this set of numbers running from $i = 1$ to $i = n$. In principle, the uncertainty associated with this mean should decrease as the number of measurements increases, and this would override any estimate of uncertainty based on a single measurement. There are two difficulties here, however. This assumes, first, that the data are distributed about the mean according to a statistical law called the normal distribution, and second, that the dataset contains a significant number of measurements. These issues will be discussed in detail in Chapters 6, 9 and 10 where the calculation of uncertainties will be dealt with in a rigorous fashion. For the present, a reasonable and straightforward approach to estimating error bars is given by the *range method*. This provides an approximate value for the error bar (the *standard error*) associated with n repeat measurements where n is less than 12 or so. To derive the standard error, we calculate the *range* of the set of measurements by identifying the largest and smallest values in the set. Then the range is divided by the number of measurements n to give the uncertainty Δx (Squires, 1985):

$$\Delta x \approx \frac{x_{\max} - x_{\min}}{n}$$

This method works best when the errors involved are truly random in origin.

Finally, care is needed when discussing "repeat measurements" as there are two ways in which these may be made. If further measurements are made on the same specimen, with no changes to the experimental arrangement, then this examines the *repeatability* of the measurement. Alternatively, if a fresh specimen is selected from a sample, e.g. a different fibre or glass fragment from the same source, or the same specimen is examined on a separate occasion or with a different instrument or settings, the *reproducibility* of the measurement is then the issue. The expectation is that the uncertainty associated with repeatability should be less than that for reproducibility.

1.3.3   Communicating uncertainty

Generally, we should quote an uncertainty rounded to one significant figure and then round the related measurement to this level of significance. This is because the uncertainty in the leading digit overrides that of any subsequent figures. In practice, an exception would be made for uncertainties starting with the digit "1", where a further figure may be quoted. This is due to the proportionally much larger difference between 0.10 and 0.15 say, compared to that between 0.50 and 0.55.

For example, a concentration measured as $0.617 \, \mathrm{mol \, dm^{-3}}$ with an estimated uncertainty of $0.032 \, \mathrm{mol \, dm^{-3}}$ should be recorded as $0.62 \pm 0.03 \, \mathrm{mol \, dm^{-3}}$, whereas with an uncertainty of $0.013 \, \mathrm{mol \, dm^{-3}}$ this should be quoted as $0.617 \pm 0.013 \, \mathrm{mol \, dm^{-3}}$.

However, if no uncertainty is given, the implied uncertainty should be in the next significant figure. For instance, if a value of $5.65 \times 10^{-6} \, \mathrm{kg}$ is quoted, it is assumed correct to the last significant figure and so the uncertainty here is in the next unquoted figure to give $5.65 \pm 0.005 \times 10^{-6} \, \mathrm{kg}$. Note that the presentation of this error in scientific notation to ensure that both the value and its uncertainty are expressed to the same power of 10. This means that the correct value is expected to be between 5.60 and 5.70 and our best estimate from measurement is 5.65. Therefore, it is very important to ensure that your value is written down to reflect clearly the precision you wish the number to have: e.g., if a length, measured using a ruler marked in mm, is exactly $20 \, \mathrm{cm}$, then it should be quoted as $20.0 \, \mathrm{cm}$, implying uncertainty to the order of tenths of a mm. It is worth noting that some scientists suggest taking a more pessimistic view of uncertainty, so that in this example of a weight quoted as $5.65 \times 10^{-6} \, \mathrm{kg}$ they would assume some uncertainty in the last figure, despite the above discussion, and work with $5.65 \pm 0.01 \times 10^{-6} \, \mathrm{kg}$. These difficulties reinforce the importance

of the experimental scientist always quoting an uncertainty at the point of the measurement itself, as estimation in retrospect is fraught with difficulty.

Worked Exercises

Exercise 1.   *Measurement of a bullet diameter is quoted as* 0.88 *cm with an uncertainty of* 0.03 *cm. Calculate the*
(a) *absolute uncertainty*   (b) *relative uncertainty*   (c) *% uncertainty.*

Solution 1.

(a) The absolute uncertainty is simply 0.03 cm.

(b) The relative uncertainty is given by $\dfrac{\Delta x}{x} = \dfrac{0.03}{0.88} = 0.034$.

(c) The % uncertainty is given by $0.034 \times 100 = 3\%$ expressed to one significant figure.

Exercise 2.   *The weight of a chemical from a three-figure balance is* 0.078 *g. Calculate the*
(a) *absolute error*   (b) *relative error*   (c) *% error.*

Solution 2.

(a) No error is quoted so the uncertainty must be in the next significant figure, to give:

$$\Delta x = 0.0005 \, \text{g}$$

(b) The relative error is given by $\dfrac{\Delta x}{x} = \dfrac{0.0005}{0.078} = 0.006$.

(c) The % error is given by $0.006 \times 100 = 0.6\%$.

Exercise 3.   *A student produces bloodstains by dropping blood droplets on to a flat paper surface and measuring the diameter of the stains produced. Five repeat measurements are carried out for each set of experimental conditions. The following is one set of results.*

		Blood droplet diameter (cm)		
1.45	1.40	1.50	1.40	1.70

Inspect this data and hence calculate a best value for the diameter and estimate the error bar.

Solution 3. All values are quoted to the nearest 0.05 cm. Four of the values are clearly tightly clustered around 1.45 cm while the fifth is 0.25 cm distant. This is likely to be an outlier and should be removed before calculating the mean:

$$\overline{x} = \frac{1.45 + 1.40 + 1.50 + 1.40}{4} = 1.44 \, \text{cm}$$

This mean is quoted to the same number of significant figures as each measurement. The error bar may be calculated by identifying the maximum and minimum values in the data and using the range method, excluding any outliers. Hence:

$$\Delta x \approx \frac{1.50 - 1.40}{4} = 0.025 \approx 0.03 \, \text{cm}$$

Thus the uncertainty may be taken as 0.03 cm and the result quoted as

$$\overline{x} = 1.44 \pm 0.03 \, \text{cm}$$

Note that there is always some approximation and rounding in such measurements, so rounding the mean to 1.45 (as all experimental values are quoted to the nearest 0.05) and quoting the uncertainty as 0.05 is acceptable in this case.

Self-assessment problems

1. Estimate the experimental uncertainty in making measurements with
   (a) a standard plastic 30 cm ruler
   (b) a small protractor
   (c) a three-digit chemical balance
   (d) a burette marked with 0.1 mL graduations.

2. Ten glass fragments are retrieved from a crime scene and the refractive index of each is measured and results quoted to five decimal places.

Refractive index
1.51826 1.51835 1.51822 1.51744 1.51752 1.51838 1.51824 1.51748 1.51833 1.51825

   It is suspected that these fragments originate from two different sources. Inspect the data, determine which and how many fragments might come from each source, then calculate the mean and estimated uncertainty for the refractive index for each.

3. Forensic science students each measure the same hair diameter using a microscope with a calibrated scale. The following results are obtained from 10 students.

Hair diameter (μm)
66   65   68   68   63   65   66   67   66   68

Determine whether there may be any possible outliers in this data and obtain a best value for the mean hair diameter together with an estimated uncertainty.

4. A chisel mark on a window frame has a measured width of 14.1 mm. Test marks are made on similar samples of wood using a suspect chisel and the following results obtained.

Width of chisel mark (mm)									
14.4	14.2	13.8	14.4	14.0	14.6	14.2	14.4	14.0	14.2

Examine this data for outliers, calculate the mean value and estimated uncertainty, and on this basis decide whether these data support the possibility that this chisel is responsible for the marks on this window frame.

1.4 Basic chemical calculations

1.4.1 The mole and molar calculations

The basic idea of the mole is to be able to quantify substances by counting the number of microscopic particles or chemical species – atoms, molecules or ions – they contain, rather than by measuring their total mass. Realistically, any sample will contain such a large number of particles that dealing directly with the numbers involved would be cumbersome and impractical in any chemical context. Instead, a new unit is defined to make manipulating quantities of chemical substances, containing these huge numbers of particles, a practical proposition. This unit is the *mole*. So, in working with quantities of substances, for example at the kg/g/mg level in mass, we count the particles in an equivalent fashion as several moles or some fraction of a mole. A formal definition of the mole is the following.

1 mole is the amount of a substance that contains the same number of entities as there are atoms in a 12 g sample of the isotope ^{12}C.

^{12}C is the most common stable isotope of carbon having 6 protons and 6 neutrons in its atomic nucleus. Strictly we should call this the gram-mole, as we have defined the mass in g rather than kg, which makes it a non-SI unit. However, although in some circumstances the kg-mole may be used, in all chemical-analytical work the g-mole predominates. You should also note the use of the word "particle" in this discussion! The mole may be applied to any entity and, within the chemical context, this will be the atom, ion or molecule. It is important, however, to be consistent, and always ensure that like is being compared with like.

Molar calculations are essentially based on proportionality, involving the conversion between mass and number of particles, as measured in moles. Hence, the constant of proportionality needs to be known. This is found by measuring very precisely the mass of one ^{12}C atom using a mass spectrometer, and from the definition of the mole, the number of particles in one mole is found to be:

$$N_A = 6.022 \times 10^{23} \text{ particles}$$

This special number, for which we use the symbol N_A, is called *Avogadro's number*. For the purposes of routine calculations this is normally expressed to two decimal places. Thus, if we have n moles of a substance that comprises N particles then:

$$N = nN_A$$

Since the number of particles N for a particular substance is proportional to its mass M, this expression may be written in an alternative way that is of great practical use, namely:

$$M = nm$$

where m is the *molar mass* or mass of one mole of the substance in grams per mole – written as $g\,mol^{-1}$. Since this is constant for any particular substance – for example, $m = 12.01\,g\,mol^{-1}$ for carbon due to the particular mix of stable isotopes in terrestrial carbon – molar masses are readily available from reference sources. For atoms or ions

the molar mass is the atomic mass (often termed the atomic weight) of a substance expressed in grams per mole.

For a molecular substance we replace the *atomic weight* by the *molecular weight* (molecular mass), which is calculated from the chemical formula using the appropriate atomic weights. If a substance comprises more than one stable isotope of any species, e.g. chlorides comprise 75.8% ^{35}Cl and 24.2% ^{37}Cl, then the molar mass must be calculated by including these in their appropriate proportions.

Worked Problems

Problem 1. *Calculate the mean molar mass of chlorine (Cl).*

Solution 1. Using the data given previously, with the isotopic masses expressed to four significant figures, the contributions from the two isotopes add proportionally to give:

$$m(Cl) = \frac{75.8}{100} \times 34.97 + \frac{24.2}{100} \times 36.97 = 35.45\,g\,mol^{-1}$$

Problem 2. *Calculate (a) the number of molecules in* 0.02 *moles of nitrogen gas (b) the number of moles that corresponds to* 3.2×10^{25} *atoms of helium.*

Solution 2. In both cases we use $N = nN_A$.

(a) $N = 0.02 \times 6.02 \times 10^{23} = 1.20 \times 10^{22}$ N_2 molecules.

(b) $N = nN_A \Rightarrow n = \frac{N}{N_A} = \frac{3.2 \times 10^{25}}{6.02 \times 10^{23}} = 53.2$ moles of He.

Problem 3. *Calculate*

(a) *the number of moles of gold (Au) present in a pure gold coin of mass* $180\,g$
(b) *the mass of 3 moles of oxygen gas* (O_2).
   [Data: molar masses are $m(Au) = 197.0\,g\,mol^{-1}$; $m(O) = 16.0\,g\,mol^{-1}$.*]*

Solution 3. In both cases we use $M = nm$

(a) $M = nm \Rightarrow n = \dfrac{M}{m} = \dfrac{180}{197.0} = 0.914$ moles of gold.

(b) $M = nm = 3 \times (2 \times 16) = 96\,g$ of O_2 gas.
   Note that as oxygen exists in diatomic molecular form we have used the molecular molar mass here.

Problem 4. *Calculate the formula mass for NaCl and hence calculate the number of moles in* $2\,g$ *of salt.* $[m(Na) = 22.99\,g\,mol^{-1}$; $m(Cl) = 35.45\,g\,mol^{-1}$.]

Solution 4. The term *formula mass* is used here since NaCl is ionic not molecular in structure, and is calculated by:

$$m(\text{NaCl}) = 22.99 + 35.45 = 58.44\,\text{g}\,\text{mol}^{-1}$$

Then, using $M = nm$, we get:

$$M = nm \Rightarrow n = \frac{M}{m} = \frac{2}{58.44} = 0.0342 \text{ moles of NaCl}$$

Problem 5. *The chemical (molecular) formula for anhydrous codeine is* $C_{18}H_{21}NO_3$. *Calculate the mass of* 0.01 *moles of the drug. [Data:* $m(C) = 12.01\,g\,mol^{-1}$; $m(H) = 1.008\,g\,mol^{-1}$; $m(N) = 14.01\,g\,mol^{-1}$; $m(O) = 16.00\,g\,mol^{-1}$, *working to four significant figures.]*

Solution 5. First we determine the molecular molar mass from the chemical formula:

$$m(\text{C}_{18}\text{H}_{21}\text{NO}_3) = 18 \times 12.01 + 21 \times 1.008 + 1 \times 14.01 + 3 \times 16.00$$
$$= 299.36\,\text{g}\,\text{mol}^{-1}$$

Then, using $M = nm$:

$$M = 0.01 \times 299.36 = 2.99\,\text{g of codeine}$$

1.4.2   Solutions and molarity

In practical, forensic chemical analysis, the concept of the mole is met with most frequently when dealing with reagents in solution and in the preparation of standards for quantitative analyses. Here it is essential to know what mass of a substance to dissolve in order to obtain a particular strength of solution, as measured by the number of chemical species (or moles) present. Conventionally, the litre or the dm^3 are used to quantify the amount of solvent (often water) included, so we should refer to the strength of such solutions using either $g\,L^{-1}$ or $g\,dm^{-3}$ when dealing with mass of solute, or $mol\,L^{-1}$ or $mol\,dm^{-3}$ in the case of the number of moles of solute. These latter units measure the *molarity* of the solution. Often, rather than using the proper full units, e.g. $2\,mol\,dm^{-3}$, we simply say that a solution is $2\,M$ or 2 molar.

The molarity of a solution is the number of moles of a substance present in $1\,dm^3$ of solution.

If n moles of the substance are dissolved in $V\,dm^3$ of solvent, the molarity C is calculated according to:

$$C = \frac{n}{V}\,mol\,dm^{-3}$$

If we need to prepare a solution of a specified molarity and volume then this formula is used to determine the number of moles of solute required, which then may be converted to mass of solute using the result from the previous section. In the analytical laboratory, reagents in common use are often kept as stock solutions, usually of a high molarity. These may then be diluted appropriately to obtain the concentration needed for a particular application. Similarly, when preparing very dilute standard solutions of known concentration for quantitative analysis, for example by ICP-OES (Inductively-Coupled-Plasma Optical Emission Spectroscopy), it is not practical to weigh out tiny amounts of solute. Rather, a more concentrated solution is first prepared, which is then diluted accordingly.

When carrying out dilution calculations, the number of moles in the system stays the same, as it is the volume of solvent and the molarity that alter. Thus we can write n in terms of either the initial concentration or final dilution:

$$C_i V_i = n = C_f V_f$$

which may be re-arranged for any of these quantities, e.g.

$$V_f = \frac{C_i V_i}{C_f}$$

1.4.3   Molality

The molarity of a solution is a measure of the concentration expressed as moles per unit volume of solvent. In situations where changes in temperature are likely, the molarity will change due to the effect of thermal expansion on this volume. An alternative is to refer the concentration to the mass of solvent, as this will be temperature independent. We refer to concentrations measured in units of moles per unit mass of solvent ($mol\,kg^{-1}$) as the *molality* of the solution. As an example, a solution

of KOH with a molality of $2\,mol\,kg^{-1}$ would be denoted as $2\,m$ KOH. The molality also differs from molarity in that it is referred to the solvent rather than to the whole solution. This means that conversion between the two requires knowledge of both the volume of solvent involved and its density.

Worked Problems

Problem 1. *A solution of NaCl in water is prepared using 5 g of salt in $250\,cm^3$ of water.*

(a) *Calculate its molarity.*
(b) *What weight of CsCl would be needed to produce a solution of the same molarity, using the same volume of water?*
(c) *If $5\,Mcm^3$ of the original solution is taken and diluted with water up to a total volume of $100\,cm^3$ what is the molarity of the new solution?*
[Data: $m(Na) = 22.99\,g\,mol^{-1}$; $m(Cs) = 132.9\,g\,mol^{-1}$; $m(Cl) = 35.45\,g\,mol^{-1}$.]

Solution 1.

(a) The formula mass of NaCl is given by $m(NaCl) = 22.99 + 35.45 = 58.44\,g\,mol^{-1}$.

The solute represents $n = \dfrac{M}{m} = \dfrac{5}{58.44} = 0.08556$ mole of NaCl.

The consequent molarity is calculated using $C = \dfrac{n}{V} = \dfrac{0.08556}{250 \times 10^{-3}} = 0.342\,mol\,dm^{-3}$.

Note the factor of 10^{-3} in the denominator to convert cm^3 to dm^3.

(b) The formula mass of CsCl is given by $m(CsCl) = 132.9 + 35.45 = 168.4\,g\,mol^{-1}$.
We require 0.08556 mol of solute for the required molarity of solution.
This corresponds to $M = nm = 0.08556 \times 168.4 = 14.4\,g$ of CsCl.

(c) The final molarity is given by $C_f = \dfrac{C_i V_i}{V_f} = \dfrac{0.342 \times 5 \times 10^{-3}}{100 \times 10^{-3}} = 0.0171\,mol\,dm^{-3}$.

Problem 2. *The enhancement of fingerprints on porous surfaces is often carried out by dipping the exhibit in ninhydrin solution. A concentrated solution of ninhydrin is first prepared using 25 g of solid dissolved in $260\,cm^3$ of solvent (ethanol, ethyl acetate and acetic acid). The working solution is then prepared by taking $50\,cm^3$ of the concentrated solution and adding further solvent up to a total volume of $1000\,cm^3$. Calculate the molarity of both the concentrated and working solutions of ninhydrin. The molecular formula for ninhydrin is $C_9H_6O_4$.*

Solution 2.   First, the molecular mass of ninhydrin is calculated using the atomic masses for the constituent atoms:

$$m(C_9H_6O_4) = 9 \times 12.01 + 6 \times 1.008 + 4 \times 16 = 178.1\,g\,mol^{-1}$$

Thus, the number of moles of ninhydrin added to the concentrated solution is:

$$n = \frac{25}{178.1} = 0.1404\,moles$$

Therefore, the molarity of the concentrated solution is given by:

$$C = \frac{n}{V} = \frac{0.1404}{260 \times 10^{-3}} = 0.540 \, \text{mol dm}^{-3}$$

When the working solution is prepared, $50 \, \text{cm}^3$ of this solution is taken. The molarity following dilution is given by:

$$C_{\text{f}} = \frac{C_i V_i}{V_{\text{f}}} = \frac{0.540 \times 50 \times 10^{-3}}{1000 \times 10^{-3}} = 0.0270 \, \text{mol dm}^{-3}$$

1.4.4 Percentage concentrations

Concentrations of solutions are often defined in terms of percentage of solute present, particularly in the biological context. There are three ways in which this may be done:

$$\% \, \text{w/w} : \frac{M_{\text{solute}}}{M_{\text{solution}}} \times 100$$

$$\% \, \text{w/v} : \frac{M_{\text{solute}}}{V_{\text{solution}}} \times 100$$

$$\% \, \text{v/v} : \frac{V_{\text{solute}}}{V_{\text{solution}}} \times 100$$

Note that all of these definitions refer to the solution and not the solvent mass or volume. The percentage concentration expressed as % w/v relates well to laboratory practice in weighing a solid then measuring liquid by volume, for example using a measuring cylinder. The last of these would be used to describe mixtures of liquids. Both w/w and v/v are dimensionless numbers and represent a true percentage as long as both numerator and denominator are measured in the same units e.g. grams or cm^3. However, % w/v is not dimensionless. The convention is to use the non-standard units of g cm^{-3}. If the solute is measured in grams and the solution specified as $100 \, \text{g}$ (or equivalently for aqueous solutions $100 \, \text{cm}^3$) then the % concentration is given directly without the need to multiply by 100. For dilute aqueous solutions % w/w and % w/v are equivalent, to all intents and purposes, as the density of the solution is approximately equal to that of water ($1.00 \, \text{g cm}^{-3}$ at room temperature).

Worked Example

Example A 2% w/v aqueous solution of cobalt isothiocyanate ($Co(SCN)_2$) is used as a presumptive test for cocaine. What mass of the salt is needed to prepare $250 \, \text{cm}^3$ of this solution?

> **Solution** This is a straightforward application of proportionality. The 2% w/v solution is defined as $2\,g$ of $Co(SCN)_2$ in $100\,cm^3$ of solution. For $250\,cm^3$ of solution we therefore require $2 \times 2.5 = 5\,g$ of the salt.

1.4.5   The mole fraction and parts per million

The concept of molarity is basically a measure of the concentration of particles in a solution, determined as moles per unit volume, but of course the solvent itself is comprised of particles e.g. molecules of water or ethanol. Hence, the concentration could be quantified instead as a ratio of particles of solute N_{solute} to the total number of particles present in the solution, $N_{solute} + N_{solvent}$ − as moles per mole. Alternatively, we could use the ratio of mass of solute to total mass of solution or even volume, for example when mixing two liquids together. All of these measures differ from that of molarity in that the units we use in our definitions are the same for both solute and solvent and so the concentration is expressed non-dimensionally, as a ratio of two numbers. The ratio of particle numbers is called the *mole fraction* X_F and may be expressed either in terms of total number of particles N or number of moles n, as:

$$X_F = \frac{N_{solute}}{N_{solvent} + N_{solute}} = \frac{n_{solute}}{n_{solvent} + n_{solute}}$$

Similarly, the mass fraction M_F and volume fraction V_F are given by:

$$M_F = \frac{M_{solute}}{M_{solvent} + M_{solute}} \text{ and } V_F = \frac{V_{solute}}{V_{solvent} + V_{solute}}$$

This method is particularly useful in describing very low concentrations and, to enhance the impact of these small numbers, we may scale the ratio to give parts per million (ppm) or parts per billion (ppb):

$$\text{ppm (mass)} \rightarrow M_F \times 10^6$$
$$\text{ppb (mass)} \rightarrow M_F \times 10^9$$

Note that, for low concentrations, the denominator is effectively the same number as that for the solvent itself. Alternatively, the mass fraction is also sometimes expressed as a percentage.

These units are used to quantify traces of substances often found as contaminants within materials or products, e.g. chemical species such as Ca^{2+}, Cl^- or HCO_3^- in mineral water. They are used also when specifying the limit of sensitivity of an analytical technique. For example, in the forensic examination of glass, the quantitative measurement of trace levels of elements such as Mn, Fe or Sr may be used to characterize and individualize each sample. Techniques exhibit differing sensitivities for this: for example, the XRF limit is often quoted as $100\,ppm$ and that for ICP-OES as down to $\sim1\,ppm$, while ICP-MS has sensitivity down to $\sim1\,ppb$.

As well as having a clear understanding of their meanings, you must be able to convert between the various concentration units so as to be able to compare measurements quoted in different ways. These are best illustrated by worked examples.

Worked Exercises

Exercise *A bottle of mineral water claims a sodium concentration of* $6.4\,mg\,dm^{-3}$. *Express this*

(a) *as a mass fraction*   (b) *in ppm (mass)*   (c) *as a mole fraction.*

Solution

(a) We need to express the volume of the solution in terms of its mass using the fact that the density of water is $1000\,\mathrm{kg\,m^{-3}}$. Thus:

$$M = \rho V = 1000 \times 1 \times 10^{-3} = 1\,\mathrm{kg}$$

Thus the mass fraction is given by:

$$M_F = \frac{M_{\mathrm{solute}}}{M_{\mathrm{solvent}} + M_{\mathrm{solute}}} = \frac{6.4 \times 10^{-6}}{1 + 6.4 \times 10^{-6}} = 6.4 \times 10^{-6}$$

Clearly this is a very dilute system and so the solute mass may be neglected in the denominator. Remember that the mass fraction is a dimensionless quantity.

(b) The ppm (mass) is given by:

$$\mathrm{ppm\ (mass)} = M_F \times 10^6 = 6.4 \times 10^{-6} \times 10^6 = 6.4\,\mathrm{ppm}$$

Note that for dilute aqueous solutions ppm (mass) and $\mathrm{mg\,dm^{-3}}$ are completely equivalent, as are ppb (mass) and $\mathrm{ng\,dm^{-3}}$.

(c) Here we must convert both the solute and solvent to moles using the molar masses: $m(\mathrm{Na})$ = $22.99\,\mathrm{g\,mol^{-1}}$ and $m(\mathrm{H_2O}) = 18.02\,\mathrm{g\,mol^{-1}}$. Thus:

$$X_F = \frac{n_{\mathrm{solute}}}{n_{\mathrm{solvent}} + n_{\mathrm{solute}}} = \frac{\left(\dfrac{6.4 \times 10^{-6}}{22.99}\right)}{\left(\dfrac{1}{18.02}\right) + \left(\dfrac{6.4 \times 10^{-6}}{22.99}\right)} = 5.04 \times 10^{-6}$$

The same result to three significant figures would be obtained by neglecting the magnitude of n_{solute} in the denominator. Note also that if the molar masses for solute and solvent are similar then M_F and X_F, and therefore ppm (mass) and ppm (moles), will be similar. However, this is not the case for quantification of heavy elements or large molecules with large molar masses; in these cases $X_F < M_F$.

Self-assessment exercises and problems

Unless otherwise stated in the question, all necessary molar masses are given in the text of Section 1.4.

1. Calculate the mean atomic mass for potassium from the following isotopic data:

$$m\left(^{39}K\right) = 38.96\,\text{g mol}^{-1}, \quad \text{abundance } 93.26\%$$

$$m\left(^{41}K\right) = 40.96\,\text{g mol}^{-1}, \quad \text{abundance } 6.74\%$$

2. For the ionic compound, KCl, calculate
   (a) the molar mass of KCl
   (b) the number of moles in 2 g of the salt
   (c) the mass corresponding to 0.15 mol
   (d) the number of atoms present in 1 g of KCl.

3. The molecular formula for paracetamol is $C_8H_9NO_2$.
   (a) Calculate the molecular mass of paracetamol.
   (b) Determine the number of moles of the drug in a 500 mg dose.

4. The HPLC analysis of the drug LSD specifies 25 mM Na_2HPO_4 as a mobile phase. If 500 cm^3 of solution are needed, calculate the mass of solute required. ($m(P) = 30.97\,\text{g mol}^{-1}$)

5. Iodine fuming is used occasionally as a means of fingerprint enhancement. The print may be made permanent by spraying with a solution of α-naphthoflavone ($C_{19}H_{12}O_2$) to produce a blue coloured image. If 350 cm^3 of solution is to be used, calculate the mass of α-naphthoflavone required to give a 0.01 M working solution.

6. Physical developer is an enhancement method for fingerprints on wet surfaces that works by the deposition of freshly made particles of colloidal silver on to the residues. One of the reagents used is a solution of $AgNO_3$ and the exhibit is pre-treated using a solution of maleic acid (molecular formula $C_4O_4H_4$).
   Calculate the molarity for solutions of (a) 10 g of $AgNO_3$ in 50 cm^3 of water
   (b) 2.5 g of maleic acid in 100 cm^3 of water.
   Data: $m(Ag) = 107.9\,\text{g mol}^{-1}$.

7. Gentian (Crystal) Violet is a substance that appears in several contexts in forensic science, one of its main uses being as an enhancement reagent for fingerprints deposited on the sticky side of adhesive tape. On submerging the exhibit in a solution of Gentian Violet, fatty deposits within the residues are dyed a deep purple colour. The molecular formula for this reagent is $C_{25}H_{30}N_3Cl$.
   (a) Calculate the molecular mass of Gentian Violet.
   (b) Calculate the mass of Gentian Violet needed to prepare a 0.2 M solution in 60 cm^3 of solvent.
   (c) If 1 cm^3 of this concentrated solution is then made up to 20 cm^3 with fresh solvent, calculate the molarity of this working solution.

8. Convert a blood alcohol level of $0.80\,\mathrm{g\,dm^{-3}}$ into the equivalent % w/w concentration, given that the density of blood is $1060\,\mathrm{kg\,m^{-3}}$.

9. A microscopic glass fragment of mass 35 ng contains 140 ppm (mass) of iron. Assume the glass is SiO_2 and taking $m(\mathrm{Si}) = 28.09\,\mathrm{g\,mol^{-1}}$ and $m(\mathrm{Fe}) = 55.84\,\mathrm{g\,mol^{-1}}$, express this concentration as
   (a) a mass fraction   (b) a mole fraction   (c) the mass of iron atoms present.

10. Quantification of diamorphine ($C_{21}H_{23}NO_5$) in heroin may be achieved using HPLC. If the minimum detectable level in solution (assumed aqueous) is found to be around $0.02\,\mathrm{mg\,cm^{-3}}$, express this
   (a) as a mass fraction   (b) in ppm (mass)   (c) as a mole fraction.

11. Standard solutions are to be prepared for the quantitative analysis of Sr in digested papers using ICP-OES. A stock solution of 0.01 M $Sr(NO_3)_2$ is available ($m(\mathrm{Sr}) = 87.62\,\mathrm{g\,mol^{-1}}$). If $1\,\mathrm{cm^3}$ aliquots of stock solution are to be diluted with deionized water, calculate, in each case, the volume of water required for dilution to the following ppm (mass) concentrations:
   (a) 100 ppm   (b) 10 ppm   (c) 1 ppm.

Chapter summary

Dealing with and communicating numerical data in a correct and clear manner is a core skill for any scientist. This includes both the representation of numbers and the choice of appropriate units. Although the SI system of units is almost universally adopted, there are several areas of the forensic discipline where non-standard units are commonly used and so conversion of units is required. Additionally, conversion calculations within the SI system need to be dealt with routinely in forensic work: for example, between $\mathrm{m\,s^{-1}}$ and $\mathrm{km\,h^{-1}}$. In acquiring and evaluating experimental data any uncertainties should be considered and included when reporting results. It is important to inspect and critically assess all such measurements for unexpected values and inconsistencies such as the presence of outliers. All forensic scientists should be competent in carrying out basic chemical calculations involving reagents and substances needed for analytical work in the chemical laboratory.