As we have already seen, water is an excellent solvent and is hardly ever found in the pure state. In this chapter, we will focus on dissolved salts. Other common dissolved substances, such as acids, bases and organic compounds, will be discussed in chapters 16 and 17.

**YOU WILL EXAMINE:**

- the importance of analysis and the difference between qualitative analysis and quantitative analysis
- protocols for obtaining water samples for analysis
- the sources of salts found in water
- a definition of a contaminant, and how contaminants may enter waterways
- how calculations can be made from chemical equations using stoichiometry
- a range of analytical techniques applicable to water samples including conductivity, colorimetry, UV–visible spectroscopy, atomic absorption spectroscopy and gravimetric analysis.

Wisdom begins in wonder.
_Socrates_

The stalactites and stalagmites in this cave were formed over thousands of years by the deposition of materials that found their way, dissolved in water, through the rocks and soil above the cave.
What is chemical analysis?

Chemical analysis is the process of determining what substances are in a sample. It also frequently involves determining the amounts of such substances. For example, it might be used to measure the masses of various elements in a compound so that its formula can be calculated. It can be used to test urine samples from athletes and racehorses to see whether they have taken any prohibited drugs. In the environment, analysis of samples can ascertain what is naturally in air and water and also identify possible contaminants. This enables statutory bodies such as the Environment Protection Agency (EPA) to set allowable limits and to impose penalties in order to protect the environment. It also allows water that might be unsuitable for one purpose to be safely used for another, thus making more efficient use of precious water resources.

Qualitative analysis finds what substances are present. Quantitative analysis measures the quantity of substance present.

Qualitative analysis

In **qualitative analysis**, the chemist is merely interested in **what** is present. In testing a urine sample from a racehorse, for example, the mere presence of a banned drug (or its metabolised products) is all that is necessary. In the confectionery industry, a sample of imported food dye might be tested to see whether it contains chemicals that are banned in this country.

Quantitative analysis

On the other hand, the question of **how much** may need to be answered — this is **quantitative analysis**. A brewer of a low alcohol beer, for example, needs to know whether its alcohol content is below a certain limit. Health authorities might need to know whether the level of mercury in samples of fish is below the allowed level.

A logical sequence often used in many analytical procedures is to perform a qualitative analysis first to find out what is present, and then to perform a quantitative analysis to find the various amounts of substances present.
Methods of chemical analysis

The analytical chemist uses methods that range from sophisticated to very simple. Techniques such as gravimetric analysis (analysing by mass) and volumetric analysis (analysing with accurate concentrations and volumes of solution) may be used. These techniques may already be familiar to you through your laboratory work. More likely, however, the analyst will use advanced instrumental techniques such as atomic absorption spectroscopy (AAS) and various types of chromatography. Due to advances in computer-chip technology, instruments for these techniques and many others have become cheaper, more powerful and more user friendly. For example, a common instrumental set-up today is to have a gas chromatograph (GC) connected to a mass spectrometer (MS) and a computer. Once the instrument has been configured and calibrated, a sample can be injected, its components identified and measured, and accurate results printed out quickly and reliably. Previously, chemists would have had to manually measure and interpret gas chromatographs from a paper printout one peak at a time, and then run a separate mass spectrum.

A technician injects a sample into a gas chromatograph. This sensitive instrument can analyse samples as small as one microlitre ($10^{-6}$ L).

Deciding on an analytical method

When deciding on a method of analysis, the properties of the substance under investigation must be considered. A chemist therefore gives careful thought to physical properties such as melting and boiling temperatures, colour and solubility. The way the substance reacts chemically is also considered. Acid-base reactions are often important, while in other cases, redox reactions might be chosen as the basis for analysis. For example, to analyse a sample of oven cleaner containing the base sodium hydroxide, an acid might be used. However, a sample of bleach containing the oxidant sodium hypochlorite would most likely be analysed by reaction against a suitable reductant. In other cases, the most appropriate method for identifying and determining a substance may be by adding something that forms a precipitate, or alternatively, something
that produces a colour that can be matched against a set of standards (colorimetric analysis).

Similarly, if instrumental analysis is being considered, the properties of the substance under test are also critical to the final choice. Many metals, for example, lend themselves to atomic absorption spectroscopy. The boiling temperature of a substance is important in distinguishing between gas chromatography and high-performance liquid chromatography if chromatographic instruments are being considered.

Another important consideration for the analyst is the degree of accuracy required. This could mean the difference between choosing a tedious but accurate method in preference to a faster but less accurate one. Is a qualitative determination all that is needed, or is a quantitative one called for? An appreciation of the strengths and weaknesses of common analytical techniques is therefore necessary, so that the most appropriate method is chosen.

Standard tests to identify substances are also important. In the analysis of an unknown compound, for example, it would be important to establish that an evolved gas is carbon dioxide rather than oxygen or hydrogen.

All the considerations above are important in designing a method of analysis. If no particular standard method suits, the chemical analyst may have to display initiative and creativity in designing a new, and maybe innovative, method to get the job done.

### Revision questions

1. Classify the following analyses as either qualitative or quantitative.
   - (a) A pregnancy test in which a chemical is added to a sample of urine and a colour change is sought
   - (b) A chlorine test in which the colour of a chemical is compared with reference standards to estimate the chlorine level in a home swimming pool
   - (c) Placement of a detector in the exhaust pipe of a car during a tune-up procedure to measure the level of carbon monoxide emissions
   - (d) Testing for monosodium glutamate, MSG, in a sample of food claimed to be 'MSG free'
2. Oil tankers need to clean residual oil from their tanks before they load new cargo. The washings are supposed to be stored on board but unscrupulous captains sometimes dump these wastes at sea to reduce costs.

   In Victoria, there have been numerous cases of such wastes washing ashore and polluting beaches. Sometimes this has occurred in the vicinity of Phillip Island and has affected its colony of fairy penguins.

   There have been instances where the analysis of such material has led to the prosecution of offending tanker captains.
   - (a) Describe how qualitative analysis might assist in such cases.
   - (b) Given that such oil is usually a complicated mixture, describe how quantitative analysis could lead to the identification of the ship causing such pollution.

### Analysing water

#### Sources of salts in water

The salts found naturally in water come from a wide variety of sources. Many minerals in the ground dissolve as the water flows over the ground or percolates through layers of rock underneath it. Salt (sodium chloride) is the most common salt found in water, and the fact that the oceans contain so much sodium chloride is evidence of this.
CHAPTER 15  Analysing water for salts

Soluble salts can hardly ever be mined because they dissolve so readily in water. They are usually found in regions with an extremely arid climate. One such region is the Atacama Desert in Chile, which has extensive deposits of Chile saltpetre (sodium nitrate, NaNO₃). This substance is rarely used these days, so many mining sites are now ghost towns, like this one in Humberstone, Chile.

It should be remembered, however, that salts do not need to dissolve in large amounts to have a significant effect on how water may be used. Good examples of this are salts of calcium such as calcium sulfate, CaSO₄, and calcium carbonate, CaCO₃. These may dissolve from minerals such as gypsum and dolomite, and rocks such as limestone and chalk, as water flows over or through them. Calcium sulfate has limited solubility in water (2.5 g L⁻¹ at normal temperatures). Calcium carbonate is virtually insoluble but reaction with water and dissolved carbon dioxide produces calcium hydrogen carbonate, which is much more soluble. The equation for this reaction is:

\[
\text{CaCO}_3(s) + \text{CO}_2(aq) + \text{H}_2\text{O}(l) \rightarrow \text{Ca(HCO}_3)_2(aq)
\]

Dissolved calcium ions, Ca²⁺, along with magnesium ions, Mg²⁺, are a major cause of hardness in water, which makes it difficult to lather and also makes it unsuitable for use in boilers and other high-temperature applications.

Human activity can also affect the levels of dissolved salts. A good example of this is the increasing salinity levels in the Murray River. Until 100 million years ago, the Murray–Darling Basin was covered by a shallow sea. After this sea retreated, the salt deposits left behind were buried underground. Since the advent of extensive irrigation, the extra water soaking into

The label on this bottle of mineral water shows the many substances that are dissolved in it. These have come from the rocks and minerals at the source of the water.
the ground has caused water tables to rise. This has brought large amounts of this previously undisturbed salt to, or near to, the surface from where it can enter rivers and streams, which eventually flow into the Murray River. The response to this problem has been the establishment of a number of salt interception schemes along the river. The graph below shows how salinity levels increased at Morgan in South Australia until 1982, but now appear to be decreasing, perhaps as a result of such schemes.

Salinity levels increased at Morgan in South Australia until 1982 but now appear to be decreasing.

Revision question
3. Explain why electrical conductivity provides a measurement of overall salt content rather than accurate values for particular salts.

Sources of contaminants in water
A contaminant can be defined as an unwanted substance that makes water unsuitable for an intended use. Both inorganic and organic contaminants enter water in many ways. These include:

- **direct discharge** from factories and other sources. This can also happen during wet weather when some older sewerage systems overflow and when ships discharge ballast water inappropriately.
- **stormwater run-off.** As water flows over the surface, it may come into contact with surface contaminants and dissolve chemicals from them in the process. It may also flow through contaminated soil, dissolving soluble components and carrying soil particles along as a suspension.
- **contaminated air contact.** Components of contaminated air may either dissolve directly in water or react with it to produce a range of undesirable chemicals.
• contact with contaminated ground water. Ground water may become contaminated when surface water comes into contact with contaminated soil and then soaks into the ground. It may also occur when leaching through old buried deposits such as landfill sites. Sometimes, the material being leached out is organic in nature and largely insoluble in water. In cases such as this it may form ‘pools’ in underground reservoirs and become a source of long-term pollution as it dissolves very slowly over many years.

### Table 15.1 Typical sources of some selected inorganic contaminants

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Sources</th>
<th>Allowable level*</th>
</tr>
</thead>
<tbody>
<tr>
<td>arsenic</td>
<td>manufacture of electrical components; wood preservatives and pesticides; gold mining; processing of ceramic materials</td>
<td>10 ppb</td>
</tr>
<tr>
<td>cadmium</td>
<td>contaminant in metals used to galvanise pipes and their subsequent erosion; metallurgical industries; improper waste disposal (e.g. nickel–cadmium batteries)</td>
<td>2 ppb</td>
</tr>
<tr>
<td>chromium</td>
<td>metallurgical processes such as alloying and electroplating; catalysts and oxidants; paint pigments</td>
<td>50 ppb</td>
</tr>
<tr>
<td>lead</td>
<td>plumbing systems; paint pigments; cable sheathing; ammunition; solder; batteries</td>
<td>10 ppm</td>
</tr>
<tr>
<td>mercury</td>
<td>mining; industrial wastes; fungicides; electrical equipment; batteries</td>
<td>1 ppb</td>
</tr>
<tr>
<td>nitrate</td>
<td>fertiliser run-off; farm animal wastes; sewage run-off</td>
<td>50 ppm (less than 3 months old) 100 ppm</td>
</tr>
<tr>
<td>sulfate</td>
<td>saltwater intrusion; mineral dissolution (e.g. CaSO₄); many industrial processes</td>
<td>250 ppm</td>
</tr>
</tbody>
</table>

*Source: Australian Drinking Water Guidelines, 2011.

**Organometallic contaminants**

A number of heavy metals can form compounds with organic molecules. While inorganic heavy metals are often only sparingly soluble, organometallic heavy metal compounds are much more soluble and can therefore enter the food chain more easily. Methyl mercury is one such example. While dimethyl mercury is virtually insoluble (and a very dangerous poison), monomethyl mercury is essentially ionic and dissolves much more readily in water. Its structure is shown on the left.

You will note from this structure that there is a covalent bond between the mercury atom and the methyl group. This is an example of a more complex type of bonding that does not fit the models that we considered in Unit 1.

The dangers of methyl mercury were first exposed in 1956 when residents of the Minamata Bay area in Japan became seriously ill after eating large amounts of fish. Many died and the effects still linger today in the form of mutations that occurred at birth. Estimates of the cumulative death toll vary but it is generally agreed to be many thousands. The source of the contamination was traced to a chemical company that had been releasing methyl mercury into the water. Methyl mercury was being used as a catalyst in the manufacture of...
Water sampling to avoid contaminants such as exhaust gases and to avoid contaminants such as exhaust gases and before, during and after sampling analytical results. These apply before, during and after the location. It would not be appropriate, for example, to take samples during a flood unless that was the specific reason for the analysis.

- **making sure the sample collected is a representative sample.** This may include sampling from a variety of locations and depths or taking samples from a location where the water is considered to be well mixed. It would also involve taking it at a time that is representative of the ‘average conditions’ for the location. It would not be appropriate, for example, to take samples during a flood unless that was the specific reason for the analysis.

- use of proper techniques in the field to prevent cross contamination

- use of equipment and procedures for storage of the samples that prevent pre- and post-collection contamination. These include the types of containers to be used, whether they are to be nearly filled or completely filled, whether they need to be rinsed before collection and even what types of lids can be used.

- collection of duplicate samples

- preservation of samples. This may involve cooling or freezing, or adding chemicals to preserve the sample. If chemicals are added, the preparation of ‘blanks’ is important; these contain everything the real sample does but are made up with distilled water rather than the sampled water. Once collected it is important that samples are analysed within certain prescribed times.

- security during transport to avoid contaminants such as exhaust gases and dust. This is important as the expected levels of contaminants in the sample may be in parts per million or even parts per billion.

- choice of appropriate analytical technique. Prescriptions exist for analysis of particular contaminants. Additionally, such tests are often required to be carried out only by suitably qualified laboratories.

The level of sophistication required can be illustrated by the collection of samples for Fe²⁺ analysis. Many metals can be collected in glass, polyethene or polypropene containers provided they are first washed with nitric acid to provide a pH between 1 and 2. However, for Fe²⁺, hydrochloric acid must be used instead, as strong nitric acid is an oxidant and may convert some of the Fe²⁺ into Fe³⁺. For the same reason, it is specified that the containers must be completely filled to exclude air, as oxygen gas is also an oxidant.

There are also a number of tests that are done ‘in the field.’ These include measurements of temperature, pH, dissolved oxygen, some anions such as fluoride and sulfate, and turbidity (cloudiness). Portable instruments are used for these tests, and these must be regularly calibrated against laboratory standards to maintain their accuracy.

**Revision question**

4. Explain why it is necessary to have strict protocols for the collection of water samples for analysis.

**A closer look at analytical methods**

As mentioned earlier in this chapter, a range of different methods exist for analysing the chemicals in a water sample. We will now take a more detailed look at some of these.
Electrical conductivity

Salts are ionic compounds; when they dissolve in water, they dissociate to produce mobile ions. This means that they can conduct electricity to an extent that depends on how many ions are present. Electrical conductivity is therefore a quick and cheap method that can be used where the total salt content of a water sample is to be measured; it does not determine which particular salts are present. It is measured in electrical conductivity units (EC). The graph on page 310 showing salinity levels at Morgan shows salinity levels in EC units.

Colorimetry

If a solution is naturally coloured, or can be coloured by adding certain chemicals, colorimetric analysis may be performed. Two common examples of this are the use of universal indicator to measure pH, where the colour produced is compared by eye with a standard chart, and estimating the level of chlorine in swimming pool water, where the sample is coloured by adding chemicals and the results compared with a chart.

More accurate results can be obtained by using an instrument called an instrumental colorimeter. This involves shining light of a complementary colour through the solution and measuring the amount absorbed.

Instrumental colorimetry is a quick method suitable for some coloured solutions. It involves shining light of a complementary colour through the solution and measuring the amount absorbed.

The water in this river contains many dissolved salts. The total amount of these salts can be measured easily using electrical conductivity.

The essential features of the colorimeter
A colour’s complement is the colour left after the original colour is removed from white light.

In a colorimeter, the detector measures the amount of light that passes through the test cell and converts this into a reading that is displayed. While normal white light can be used, more accurate results are obtained if light that is complementary to the colour in the test cell is used. When light of a particular colour is removed from white light, the remaining light produces a different colour. The second colour is said to be complementary to the original colour. For example, if copper sulfate levels are being measured, the best colour to shine through such samples is red light.

### TABLE 15.2 Observed colours and their complementary colours

<table>
<thead>
<tr>
<th>Colour observed</th>
<th>Colour absorbed</th>
<th>Frequency of absorbed colour ($\times 10^{14}$ Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>green</td>
<td>deep red</td>
<td>3.85–4.41</td>
</tr>
<tr>
<td>blue-green</td>
<td>red</td>
<td>4.41–4.83</td>
</tr>
<tr>
<td>blue</td>
<td>orange</td>
<td>4.83–5.17</td>
</tr>
<tr>
<td>blue-violet</td>
<td>yellow</td>
<td>5.17–5.45</td>
</tr>
<tr>
<td>violet</td>
<td>yellow-green</td>
<td>5.45–5.76</td>
</tr>
<tr>
<td>deep red</td>
<td>green</td>
<td>5.76–6.00</td>
</tr>
<tr>
<td>red</td>
<td>blue-green</td>
<td>6.00–6.38</td>
</tr>
<tr>
<td>orange</td>
<td>blue</td>
<td>6.38–6.81</td>
</tr>
<tr>
<td>yellow</td>
<td>blue-violet</td>
<td>6.81–7.14</td>
</tr>
<tr>
<td>yellow-green</td>
<td>violet</td>
<td>7.14–7.89</td>
</tr>
</tbody>
</table>

Colorimetry is relatively cheap and is obviously useful for measuring the concentration of a coloured species (or a colourless species from which a coloured derivative can be easily prepared). Its major drawback is that care must be taken to ensure that no other coloured species are present in a sample that could also absorb the particular colour of light being used. This method can produce results to within 1–2% accuracy.

UV-visible spectrometry and atomic absorption spectrometry are two further methods that can be used if more accurate results are required.

### Determining phosphate levels — an example of colorimetry in use

Phosphates are important nutrients for plants but can become an environmental problem when they enter water systems in large amounts. As we have already seen, this can lead to eutrophication if certain other conditions are present as well. Sources of phosphate include fertilisers such as ammonium phosphates (typically $(\text{NH}_4)_2\text{HPO}_4$ and/or $(\text{NH}_4)_3\text{HPO}_4$) and superphosphate (a mixture of calcium dihydrogen phosphate, $\text{Ca(H}_2\text{PO}_4)_2$, and calcium sulfate, $\text{CaSO}_4$), which are applied in large amounts as part of current agricultural practices. Until recently, laundry detergents were another source of this nutrient; they were added to remove hardness and buffer the wash water to maintain a slightly alkaline pH. Environmental awareness by consumers, however, has now led to phosphate removal from virtually all such detergents.

Testing for phosphate levels is a relatively easy application of colorimetry. The process involves the addition of ammonium molybdate, a chemical that forms a blue compound if phosphate is present. The more phosphate, the more intense the blue colour of the solution. If a set of standards containing known phosphate levels is produced in the same way as the unknown, the level in the
Atomic absorption spectroscopy measures the absorption of light at a particular frequency. It is suitable for coloured solutions, solutions that can be made coloured, and solutions that absorb in the ultraviolet region.

UV-visible spectroscopy measures the absorption of light at a particular frequency. It is suitable for coloured solutions, solutions that can be made coloured, and solutions that absorb in the ultraviolet region.

**Atomic absorption spectroscopy**

Atomic absorption spectroscopy is suitable for the detection of many metals and metalloids. Atoms of a particular element, when energised in a flame, absorb light from an emission lamp containing that same element.

UV-visible spectroscopy is a more sophisticated development of instrumental colorimetry. The basic idea is the same — the amount of absorption is related to the concentration of the substance being tested. However, this technique is far more selective and therefore less likely to suffer interference from similarly coloured compounds. This is because light of a specific frequency is used. For example, although two compounds in a sample to be tested appear blue, one of these might absorb strongly at a frequency that the other does not. This frequency can then be used in the subsequent analysis to distinguish between them.

Just as many substances absorb light from the visible section of the electromagnetic spectrum (and therefore appear coloured), there are also substances that absorb radiation from the ultraviolet region of the spectrum. As our eyes are not able to detect this radiation, substances absorbing in this region may not necessarily appear coloured. UV-visible spectroscopy is therefore suitable for many colourless substances as well as coloured ones.

The UV-visible spectrophotometer can be used both qualitatively and quantitatively.

For qualitative analysis, the sample to be analysed is dissolved using a suitable solvent. A spectrum is obtained by measuring the absorbance against a range of frequencies. This spectrum can then be compared to known spectra for the suspected substances in the sample. In practice, UV-visible spectroscopy is used only as supporting evidence in an identification, not as a qualitative analysis method in its own right.

In quantitative analysis, a pure sample of the substance to be measured would first have its spectrum determined as described above. From this spectrum, a frequency would be chosen at which strong absorption occurs. The absorbance of the test sample at this frequency would then be compared to the absorbance of a suitable standard. For example, to measure the level of glucose in a sample of urine, the spectrum of pure glucose would be obtained and a suitable frequency chosen. Glucose samples of known concentration would then be tested at this chosen frequency and their absorbances noted. Finally, the sample of urine would be tested and the absorbance compared to that of the standards to obtain the glucose concentration. Note that in choosing a suitable frequency for such an analysis, care must be taken to choose a frequency at which the glucose in the urine is the only substance that absorbs.

**Atomic absorption spectroscopy (AAS)**

Atomic absorption spectroscopy, which was developed in Australia by the CSIRO, is useful for detecting the presence of metal ions.

The instrument used is called an atomic absorption spectrometer. It uses the absorption of light to measure concentrations of metal ions. It works on the principle that atoms absorb light if the frequency (and therefore the energy) of this light is of the correct value to promote an electron from its ground state energy level to a higher energy level.

Solutions of known concentration are analysed first, followed by the solution being tested. These solutions are drawn into the flame. A lamp is used to shine light of a very specific wavelength through the flame towards a detector. The amount of light absorbed by the flame is measured and can be used to determine the concentration of the substance being analysed.
The flame is usually an air/acetylene, $\text{C}_2\text{H}_2$, mixture. However, for some analyses a hotter flame is required. In such cases nitrous oxide, $\text{N}_2\text{O}$, may be added to the gas mixture.

This technique is both very sensitive as well as being very selective. Concentrations of parts per million are easily measured, and, for some ions, parts per billion. The selectivity of the instrument allows a particular component of a mixture to be analysed without having to separate it from other components. For example, the proportions of sodium and potassium in a salt substitute can be measured without one ion affecting the other. This selectivity is due to the frequency of the light from the lamp. If, for example, a lamp is used that emits light at a frequency found in the sodium spectrum but not the spectrum of potassium, only the sodium atoms in the flame absorb the light. The sodium content can thus be measured with no interference from the potassium.

## Sample problem 15.1

A sample of drinking water was collected for analysis of its sodium (ion) content.

Immediately prior to analysis by AAS, it was diluted by the addition of an equal volume of deionised water.

Use the results to determine the level of sodium in the original sample.

**Solution:** A set of sodium standards were analysed, followed by the diluted sample. The results are shown in table 15.3.
For quantitative use, both instrumental colorimetry and atomic absorption spectroscopy require calibration by taking readings from a set of known standards.

A calibration curve was produced from these results, as shown below. Reading the absorbance value off this graph revealed that the test sample had a concentration of 13.5 ppm.

Therefore, from the calibration curve:

\[ \text{concentration (diluted sample)} = 13.5 \text{ ppm} \]

The original sample was diluted by a factor of 2, so:

\[ \text{concentration (undiluted sample)} = 13.5 \times 2 = 27 \text{ ppm} \]

*Note:* 27 ppm is the same as 27 mg L\(^{-1}\).

Such a level may need to be taken into account for people on low-sodium diets.

### Revision question

5. A second sample of water suspected to contain a higher level of sodium was analysed on the same instrument as in sample problem 15.1, using the same standards. Due to its suspected higher level of sodium, it was diluted by adding 90 mL of deionised water to a 10 mL sample of the sampled water. AAS produced a reading of 0.790 from the diluted sample. What is the concentration of sodium (in mg L\(^{-1}\)) of this sample?

### Gravimetric analysis

Gravimetric analysis is analysis by weight. Among other steps, it involves collecting and drying precipitates, and then weighing them. In order to understand the calculations involved, it is important to know how chemical equations can be used to calculate masses of reactants and products involved in chemical reactions.

We will now consider this important topic before returning to a more detailed look at gravimetric analysis.
Stoichiometry—calculations using balanced equations

How is chemistry involved in the operation of an automotive airbag? Before being inflated, airbags contain a small amount of solid sodium azide, NaN₃. On impact with another vehicle or object, an electric spark is released, acting as a trigger. Very quickly, the sodium azide in the airbag decomposes to form solid sodium, Na, and nitrogen gas, N₂, according to the chemical equation:

$$2\text{NaN}_3(s) \rightarrow 2\text{Na}(s) + 3\text{N}_2(g)$$

The sodium then reacts with water vapour in air. The nitrogen gas produced in the reaction inflates the airbag in time to absorb much of the impact energy of the crash, which may otherwise have caused injury to the driver. The sodium azide reaction must produce just the right amount of nitrogen gas to inflate the bag to the correct pressure. How do designers know how much sodium azide to use so that the airbag is correctly inflated? They use stoichiometric calculations.

The study of relative amounts — ratios — of substances involved in chemical reactions is known as stoichiometry. The word ‘stoichiometry’ comes from two Greek words meaning ‘element’ and ‘measure’. Knowledge of stoichiometry is essential whenever quantitative information about a chemical reaction is required.

Stoichiometry is used every day in the home and in industry. Baking a cake in the kitchen requires a recipe to ensure proper quantities of all ingredients are used. Imagine how a cake would taste if a chef added three times the required amount of flour! Many cooks have disasters in the kitchen by not using ingredients in the correct ratios. On a larger scale, an industrial chemist reducing iron in a blast furnace needs to know exactly how much iron ore, Fe₂O₃, coke, C, and limestone (calcium carbonate), CaCO₃, to feed into the top of the furnace in order to produce a certain amount of iron. A disaster in industry can be life threatening because incorrect ratios of chemicals can result in uncontrolled, violent explosions.

Solving stoichiometric problems is particularly important in fields such as food chemistry, drug chemistry, forensic science and in any industry where chemicals are manufactured. Stoichiometry may be thought of as the means of obtaining a recipe for a chemical reaction.

What a balanced chemical equation tells us

Chemically speaking, if we wish to say, ‘One molecule of nitrogen gas reacts with three molecules of hydrogen gas to form two molecules of ammonia gas’, we simply write:

$$\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$$

However, it would be impossible and impractical to make ammonia molecule by molecule. Chemists work with larger quantities called moles (symbol mol). The coefficients in a balanced chemical equation tell us the relative numbers of moles of reactants and products taking part in the reaction. For example, 1 mole of nitrogen gas reacts with 3 moles of hydrogen gas to produce 2 moles of ammonia gas.

The equation actually indicates the mole ratio of reactants and products. The beauty of this method is that the ratios never change. If 1 mole of nitrogen reacts with 3 moles of hydrogen, then 2 moles of nitrogen reacts with 6 moles of hydrogen, 0.5 mole of nitrogen reacts with 1.5 moles of hydrogen, and so on.

Assuming that there is plenty of nitrogen, how much ammonia is produced by 3 moles of hydrogen? The equation tells us: 2 moles of ammonia. Similarly, 6 moles of hydrogen produces 4 moles of ammonia.
An equation also tells us about the ratio between other quantities of the reactants and the products including the number of particles and the masses of the reactants and products.

So, when 1 mole of N₂ gas reacts with 3 moles of H₂ gas to produce 2 moles of NH₃ gas, we know that this can be restated as: 28 g of N₂ gas (or 6.02 × 10²³ N₂ molecules) reacts with 6 g of H₂ gas (or 1.806 × 10²⁴ H₂ molecules) to produce 34 g of NH₃ gas (or 1.204 × 10²⁴ NH₃ molecules).

**What a chemical equation does not tell us**

An equation conveys no information about the rate of a reaction. It may be fast, as in the explosive oxidation of hydrogen to form water, or it may be slow, as in the oxidation or rusting of iron.

An equation does not tell us whether a reaction requires heat or gives off heat, or what temperature or pressure is needed.

Finally, an equation gives no details as to how the individual atoms or molecules are transformed from reactants to products. This information is essential for full understanding of how a chemical reaction takes place.

Different fuels are suited for different purposes. High-performance racing cars may run on diesel, ethanol, methanol or petrol. All of these fuels react in oxygen to produce carbon dioxide and water vapour.

**Sample problem 15.2**

Methanol, CH₃OH, is used as a fuel in some racing cars. The equation for the combustion of methanol in the car’s engine is:

\[ 2\text{CH}_3\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 4\text{H}_2\text{O}(g) \]

(a) How many moles of oxygen are needed to react with 4 moles of methanol?
(b) How many moles of water are formed when 1 mole of oxygen reacts completely with methanol?
Mass–mass stoichiometry involves calculating the mass of one of the substances in a reaction by using the equation and the mass of one of the other substances. The steps are:

- Write a balanced equation, identifying the known and unknown quantities.
- Change known mass into moles.
- From the equation, use the molar ratio to predict the moles of the required substance.
- Change the moles into mass of the required substance.

Solution:
(a) The equation tells us that 2 moles of methanol reacts with exactly 3 moles of oxygen. Use this ratio (2 : 3) to calculate that 4 moles of methanol reacts with 6 moles of oxygen exactly.
(b) The equation tells us that 3 moles of oxygen produces 4 moles of water. Use the ratio (3 : 4) to conclude that 1 mole of oxygen produces $\frac{4}{3}$ moles of water.

Revision questions
6. Silver tarnishes partly because of the presence of small amounts of hydrogen sulfide, $\text{H}_2\text{S}$ (a gas that originates from the decay of food and smells like rotten eggs), according to the reaction:

$$4\text{Ag(s)} + 2\text{H}_2\text{S(g)} + \text{O}_2(g) \rightarrow 2\text{Ag}_2\text{S(s)} + 2\text{H}_2\text{O(l)}$$

(a) How many moles of silver sulfide form from the complete reaction of 1 mole of silver?
(b) How many moles of hydrogen sulfide react with 1 mole of silver?
(c) How many moles of silver sulfide form from 3.5 moles of hydrogen sulfide?

7. Methane is the main component of the natural gas that we use as a fuel. When methane burns in air, the following reaction takes place:

$$\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O(g)}$$

(a) How many moles of methane are needed to react with 1 mole of oxygen gas?
(b) How many moles of oxygen are needed to react with 0.1 moles of methane?
(c) How many moles of carbon dioxide are produced from 0.1 moles of methane?
(d) How many moles of water are produced from 0.1 moles of methane?
(e) How many moles of carbon dioxide are produced by 0.1 moles of oxygen gas?
(f) How many moles of oxygen gas react completely with 0.25 moles of methane?
(g) How many moles of water are produced from 8 moles of oxygen gas?

Mass–mass stoichiometry

Mass–mass stoichiometry involves solving a problem in which the mass of a reactant or product is given. You are then asked to calculate the mass of another reactant or product. Mass–mass stoichiometry requires the conversion of masses of substances to moles, or moles of substances to masses. Such conversions make use of the formulas:

$$\text{moles(n)} = \frac{\text{mass (m)}}{\text{molar mass (M)}}$$

$$\text{mass (m)} = \text{moles(n)} \times \text{molar mass (M)}$$

Mass–mass stoichiometric problems can be solved in four steps:
1. Write a balanced chemical equation for the reaction, identifying the known (given) and unknown (required) quantities of substance.
2. Calculate the number of moles of the known quantity of substance present.
3. From the equation, find the molar ratio that states the proportion of known to unknown quantities in the reaction and use it to calculate the number of moles of the required substance.
4. Calculate the quantity (mass) of the required substance.
Sample problem 15.3

Some sulfur is present in coal in the form of pyrites, FeS₂. This substance is also known as ‘fool’s gold.’ When pyrites burns, it pollutes the air with one of its combustion products, sulfur dioxide, and produces solid iron(III) oxide. What mass of iron(III) oxide is formed from the complete combustion of 183.5 g of pyrites?

Solution:

STEP 1
Write the equation, identifying the known and unknown quantities of substance.

\[
4\text{FeS}_2(s) + 11\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s) + 8\text{SO}_2(g)
\]

Pyrites is the known quantity and iron(III) oxide is the unknown quantity.

STEP 2
Calculate the number of moles of the known quantity of substance, FeS₂.

\[
n(\text{FeS}_2) = \frac{183.5}{55.8 + (2 \times 32.1)}
\]

\[
= \frac{183.5}{120.0}
\]

\[
= 1.529 \text{ mol}
\]

STEP 3
Find the molar ratio, FeS₂:Fe₂O₃, from the equation, and use it to calculate the number of moles of the required substance, Fe₂O₃.

The ratio is 4 : 2, which becomes 2 : 1.

\[
n(\text{Fe}_2\text{O}_3) = \frac{2}{4} n(\text{FeS}_2) = \frac{n(\text{FeS}_2)}{2}
\]

\[
= \frac{1.529}{2}
\]

\[
= 0.7643 \text{ mol}
\]

STEP 4
Calculate the required quantity (mass) of Fe₂O₃ formed by the reaction.

\[
m(\text{Fe}_2\text{O}_3) = n \times M
\]

\[
= 0.7643 \times (2 \times 55.8 + 3 \times 16.0)
\]

\[
= 122.0 \text{ g}
\]

Revision questions

8. Calculate the mass of water that is produced when 2.8 g of methane is burned in air.

9. Propane burns in air according to the equation:

\[
\text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(g)
\]

(a) What mass of water is produced by 6.5 g of oxygen?
(b) What mass of O₂ reacts with 1.7 g of C₃H₈?
(c) What mass of CO₂ is produced by 0.50 moles of propane gas, C₃H₈?
(d) How many grams of propane gas are needed to produce 5.92 g of CO₂(g)?
(e) How many kilograms of CO₂(g) are released into the atmosphere when the entire contents of a 5.0 kg cylinder of propane are used at a barbecue?
10. When 2.864 g of potassium iodide reacts completely with a solution of lead nitrate solution, a yellow precipitate of lead iodide forms according to the following equation:

\[ 2\text{KI(s)} + \text{Pb(NO}_3\text{)}_2(\text{aq}) \rightarrow \text{PbI}_2(\text{s}) + 2\text{KNO}_3(\text{aq}) \]

Calculate the mass of lead iodide that precipitates.

11. A solution is made by dissolving an unknown amount of barium chloride in water. It is then added to a solution of potassium carbonate such that all the barium chloride reacts. The equation for this reaction is:

\[ \text{K}_2\text{CO}_3(\text{aq}) + \text{BaCl}_2(\text{aq}) \rightarrow 2\text{KCl(}\text{aq}) + \text{BaCO}_3(\text{s}) \]

(a) What information in the equation tells you that barium carbonate is a precipitate?

(b) If 4.582 g of barium carbonate is formed, calculate the mass of barium chloride that was originally dissolved.

12. Industrially, metallic iron may be obtained from an ore such as haematite, \( \text{Fe}_2\text{O}_3 \), after reaction in a blast furnace according to the equation:

\[ \text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO(g)} \rightarrow 2\text{Fe(l)} + 3\text{CO}_2(\text{g}) \]

Use a spreadsheet program or a graphics calculator to set up a spreadsheet to calculate the mass of iron that may be formed by this reaction, given an initial mass of haematite. The following template can be used as the basis for your spreadsheet.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mass of</td>
<td>moles of</td>
<td>moles of</td>
<td>mass of</td>
</tr>
<tr>
<td>haematite used</td>
<td>haematite</td>
<td>iron formed</td>
<td>iron formed (g)</td>
</tr>
<tr>
<td>(g)</td>
<td>formed</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- In cell B2, type = A2/159.7. Then click and drag from the bottom right corner of the cell down the column to fill the column.
- In cell C2, type = 2'B2. Then click and drag from the bottom right corner of the cell down the column to fill the column.
- In cell D2, type = C2'55.85. Then click and drag from the bottom right corner of the cell down the column to fill the column.

Once your spreadsheet has been set up, you can enter values for the mass of haematite used in the reaction, and let your spreadsheet calculate the amount of iron you would expect to be produced.

(a) What mass of iron would be produced by 23.7 kg of haematite?

(b) Explain the formulas set up in cells B2, C2 and D2.

(c) Add columns to your spreadsheet to calculate the mass of carbon dioxide that may be formed in the reaction.

(d) What mass of carbon dioxide would be produced by 805 kg of haematite?

**Limiting reactant calculations**

When the amounts of reactants provided for a reaction are not in the mole ratio, amounts of one or more reactants are left over once the reaction has taken place.

The amounts of the products are limited by the amount of the reactant that is completely used up in the reaction. Let’s return to our previous example:

\[ \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g}) \]

Recall that a balanced equation indicates the mole ratios in which the reactants are used up and the products are formed. According to this equation,
1 mole of nitrogen gas reacts with 3 moles of hydrogen gas to produce 2 moles of ammonia gas.

If 1 mole of nitrogen and 4 moles of hydrogen are mixed and allowed to react, then all the nitrogen and 3 moles of hydrogen are used up. This means that 1 mole of hydrogen is left over. The reactant that is completely used up (in this case nitrogen) is called the limiting reactant. Any unreacted reactants (hydrogen in this example) are called excess reactants. The amount of product formed by the reaction is limited by the amount of the limiting reactant. In this case, the addition of more hydrogen to the mixture would have no effect on the amount of product formed, as there is no more nitrogen available to react with it.

Sample problem 15.4

Magnesium and oxygen react to form magnesium oxide according to the following equation:

\[ 2\text{Mg(s)} + \text{O}_2(\text{g}) \rightarrow 2\text{MgO(s)} \]

If 24.31 g of magnesium and 20.00 g of oxygen are available for reaction, determine the limiting reactant, the reactant in excess and by how many moles, and the mass of magnesium oxide formed.

Solution:  

STEP 1  
Convert the given information to moles.

\[ n(\text{Mg}) = \frac{24.3}{24.3} = 1.00 \text{ mol} \]
\[ n(\text{O}_2) = \frac{20.00}{32.0} = 0.625 \text{ mol} \]

STEP 2  
Compare this mole ratio with the mole ratio in the equation. According to the equation, 2 mol of magnesium reacts with 1 mol of oxygen. Therefore, if 1.00 mol of Mg were to react we would need 0.500 mol of O\textsubscript{2}. We have 0.625 mol O\textsubscript{2}, which is more than enough. Therefore, Mg is the limiting reactant.

STEP 3  
The amount of product formed is determined by the amount of limiting reactant. According to the equation, 2 mol of magnesium produces 2 mol of magnesium oxide. Therefore, 1.00 mol Mg would produce 1.00 mol MgO.

STEP 4  
Calculate the mass of MgO produced.

\[ m = 1.00 \times M(\text{MgO}) \]
\[ = 1.00 \times 40.3 \]
\[ = 40.3 \text{ g} \]

Mass–concentration stoichiometry

Many chemical reactions involve interactions between solids and solutions. These reactions may be referred to as mass–concentration stoichiometry. Two solutions may be mixed to form a precipitate, or solids may dissolve in some solutions to form new products. Stoichiometric calculations that involve solids and solutions require the use of two formulas to calculate moles. When dealing with solids, we use the formula:

\[ n = \frac{m}{M} \]
When dealing with solutions, we use the formula:
\[ n = cV \]

Mass–concentration stoichiometric problems may be solved in four steps:
1. Write a balanced chemical equation for the reaction, identifying the known (given) and unknown (required) quantities of substance.
2. Calculate the number of moles of the known quantity of substance present.
3. From the equation, find the molar ratio that states the proportion of known to unknown quantities in the reaction and use it to calculate the number of moles of the required substance.
4. Calculate the quantity of the required substance.

Note that these steps are essentially the same as for solving mass–mass stoichiometry problems.

**Sample problem 15.5**

Hydrofluoric acid etches glass and quartz according to the reaction:

\[ \text{SiO}_2(s) + 4\text{HF(aq)} \rightarrow \text{SiF}_4(g) + 2\text{H}_2\text{O(l)} \]

A quartz sculptor has a 500 mL container of 22.50 M hydrofluoric acid. What mass of quartz could be etched by the acid?

**Solution:**

**STEP 1**

Write the equation, identifying the known and unknown quantities of substance.

\[ \text{SiO}_2(s) + 4\text{HF(aq)} \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O(1)} \]

**STEP 2**

Calculate the number of moles of the known quantity of substance.

\[ n(\text{HF}) = cV \]
\[ = 22.50 \times 0.500 \]
\[ = 11.3 \text{ mol} \]

**STEP 3**

Find the molar ratio from the equation and use it to calculate the number of moles of \( \text{SiO}_2 \) required.

\[ n(\text{SiO}_2) : n(\text{HF}) \text{ is } 1 : 4 \]
\[ n(\text{SiO}_2) = \frac{1}{4} n(\text{HF}) \]
\[ = 2.81 \text{ mol} \]

**STEP 4**

Calculate the required quantity of \( \text{SiO}_2 \), using \( m = n \times M \).

\[ m = 2.81 \times (28.1 + 2 \times 16.0) \]
\[ = 169 \text{ g} \]

**Sample problem 15.6**

A piece of aluminium is placed in a beaker containing 500 mL of \( \text{H}_2\text{SO}_4 \) solution and hydrogen gas is evolved. Given that the initial mass of Al was 15.14 g and its final mass was 9.74 g, calculate the concentration of the acid.

**Solution:**

**STEP 1**

Write the equation, identifying the known and unknown quantities of substance.

\[ 2\text{Al(s)} + 3\text{H}_2\text{SO}_4(aq) \rightarrow \text{Al}_2(\text{SO}_4)_3(aq) + 6\text{H}_2(g) \]

**Note:**

Involves the same steps as mass–mass stoichiometry, except that the formula \( n = cV \) is used.

### Sample problem 15.6

A piece of aluminium is placed in a beaker containing 500 mL of \( \text{H}_2\text{SO}_4 \) solution and hydrogen gas is evolved. Given that the initial mass of Al was 15.14 g and its final mass was 9.74 g, calculate the concentration of the acid.

**Solution:**

**STEP 1**

Write the equation, identifying the known and unknown quantities of substance.

\[ 2\text{Al(s)} + 3\text{H}_2\text{SO}_4(aq) \rightarrow \text{Al}_2(\text{SO}_4)_3(aq) + 6\text{H}_2(g) \]

**Note:**

Involves the same steps as mass–mass stoichiometry, except that the formula \( n = cV \) is used.
**STEP 2**
Determine the mass of Al that was used in the reaction and calculate the number of moles this mass represents.

\[ m(\text{Al}) = 15.14 - 9.74 = 5.40 \text{ g} \]

\[ n(\text{Al}) = \frac{5.40}{27.0} = 0.200 \text{ mol} \]

**STEP 3**
Find the molar ratio from the equation and use it to calculate the number of moles of H\text{2SO}_4 required.

\[ n(\text{H}_2\text{SO}_4) : n(\text{Al}) = 3 : 2 \]

\[ n(\text{H}_2\text{SO}_4) = \frac{3}{2} n(\text{Al}) = \frac{3}{2} \times 0.200 = 0.300 \text{ mol} \]

**STEP 4**
Calculate the concentration of the H\text{2SO}_4 required for the reaction.

\[ c(\text{H}_2\text{SO}_4) = \frac{n}{V} = \frac{0.300}{0.500} = 0.600 \text{ M} \]

**Revision questions**

13. Zinc metal is reacted with 400 mL of a 0.250 M solution of sulfuric acid, H\text{2SO}_4. Calculate the mass of zinc sulfate formed.

14. Consider the following balanced equation:

\[ \text{Cd(NO}_3\text{)}_2(aq) + \text{Na}_2\text{S(aq)} \rightarrow \text{CdS(s)} + 2\text{NaNO}_3(aq) \]

(a) Calculate the mass of CdS produced from 235 mL of a 0.178 M solution of Na\text{2S} with excess Cd(NO\text{3})\text{2} present.

(b) What is the significance of Cd(NO\text{3})\text{2} being present in excess?

15. In a laboratory experiment, a strip of magnesium weighing 2.56 g was placed into 200 mL of a hydrochloric acid solution. Bubbles of gas were observed and identified as hydrogen. The next day, no bubbles were observed in the beaker so the magnesium strip was removed from the beaker, dried and reweighed. Its mass was recorded as 0.350 g.

(a) Why were no bubbles observed in the beaker on the second day of the experiment?

(b) Calculate the concentration of the acid.

(c) Identify the sources of error in this experiment.

(d) Outline the safety precautions that should be taken in this experiment.

**Gravimetric analysis**

Gravimetric analysis is a form of quantitative analysis. It is analysis by mass.
be used quickly to check whether this practice has occurred. In the area of agriculture, a soil scientist often needs to know the moisture content of a soil sample in order to determine the effectiveness of various soil conditioning procedures.

Gravimetric analysis can also be a much more sophisticated procedure in which knowledge of chemical reactions, solubilities and stoichiometry is used to determine the amount of a substance in a sample. Using chemical knowledge in this way makes gravimetric analysis a powerful tool that can be used by analytical chemists in a wide range of situations.

**Analysing for water content**

This simple procedure involves weighing an initial sample and then placing it in an oven at 110 °C. After heating, the sample is reweighed and then put back in the oven. Naturally it will weigh less due to the evaporation of some water. This cycle of heating and weighing is then repeated until no further decrease in mass is noted. This is called ‘weighing to constant mass’ and indicates that all the water in the sample has evaporated.

**Sample problem 15.7**

A 23.1 g sample of soil is heated to 105 °C for 60 minutes. It is then weighed and the process repeated a number of times. A mass of 21.0 g is eventually obtained, which does not change upon further heating.

Calculate the percentage of water in this sample of soil.

The mass of water lost from the sample is 23.1 – 21.0 = 2.1 g.

The percentage of water in the sample is therefore $\frac{2.1}{23.1} \times 100 = 9.1\%$.

**Extending the gravimetric method**

A more sophisticated version of gravimetric analysis can be used to quantitatively determine a component in a solid mixture.

In this procedure, the sample being analysed is usually dissolved in water and then treated with a chemical that forms a precipitate. (It is this precipitate that removes the ions required from solution so that the amount of ions may later be determined.) This precipitate is then carefully collected (usually by filtration), dried and weighed to constant mass as described earlier. From this mass and the original mass of material dissolved, the component may be determined quantitatively.

Gravimetric analysis often involves the following steps:

(a) weighing the sample to be analysed; (b) dissolving the sample in water; (c) adding a suitable chemical to form a precipitate; (d) filtering to collect the precipitate; and (e) repeated drying and weighing until a constant mass of precipitate is obtained.

*Note:* Sometimes, the substance being analysed is already dissolved, as with water samples. In such cases, the method starts at step (c).
This procedure is especially suitable for determining metal ions. It is also very useful for determining anions such as sulfate, which form some easily prepared insoluble salts (such as barium sulfate).

When designing a gravimetric procedure, a knowledge of the solubilities of the precipitates likely to be produced is important.

### TABLE 15.4 The solubility in water of compounds of common anions

<table>
<thead>
<tr>
<th>Anion</th>
<th>Cations forming soluble compounds</th>
<th>Cations forming insoluble compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrates</td>
<td>all</td>
<td>—</td>
</tr>
<tr>
<td>chlorides</td>
<td>most</td>
<td>Ag⁺, Pb²⁺</td>
</tr>
<tr>
<td>bromides</td>
<td>most</td>
<td>(PbCl₂ is moderately soluble in hot water.)</td>
</tr>
<tr>
<td>iodides</td>
<td>most</td>
<td>Ba²⁺, Pb²⁺</td>
</tr>
<tr>
<td>sulfates</td>
<td>most</td>
<td>(Ag₂SO₄ and CaSO₄ are slightly soluble.)</td>
</tr>
<tr>
<td>carbonates</td>
<td>Na⁺, K⁺, NH₄⁺</td>
<td>most</td>
</tr>
<tr>
<td>phosphates</td>
<td>Na⁺, K⁺, NH₄⁺</td>
<td>most</td>
</tr>
<tr>
<td>sulfides</td>
<td>Na⁺, K⁺, NH₄⁺</td>
<td>most</td>
</tr>
<tr>
<td>hydroxides and oxides</td>
<td>Na⁺, K⁺, Ba²⁺</td>
<td>most</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Ca(OH)₂ is slightly soluble.)</td>
</tr>
</tbody>
</table>

### Sample problem 15.8

A pharmaceutical company wishes to test the purity of some commercial barium chloride.

A sample of the commercial barium chloride was weighed and found to have a mass of 10.0 g. After dissolving in water, excess sulfuric acid was then added to form a precipitate of barium sulfate. This precipitate was then filtered, dried and weighed. It was found to have a mass of 10.05 g.

Calculate the percentage purity of the barium chloride.

**Solution:**

The equation for the formation of the precipitate is:

\[
\text{BaCl}_2(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2\text{HCl}(\text{aq})
\]

\[
m(\text{BaSO}_4) = 10.55 \text{ g} \\
M(\text{BaSO}_4) = 233.4 \text{ g mol}^{-1}
\]

\[
\therefore n(\text{BaSO}_4) = \frac{10.55}{233.4} = 0.04520 \text{ mol}
\]

\[
\therefore n(\text{BaCl}_2) = 0.04520 \text{ mol}
\]

\[
\therefore m(\text{BaCl}_2) = 0.04522 \times 208.3 \text{ g}
\]

\[
= 9.415 \text{ g}
\]

\[
\therefore \text{ percentage barium chloride (in original sample)} = \frac{9.415}{10.0} \times 100 = 94.2\%
\]

### Sample problem 15.9

A sample of groundwater from an old lead battery manufacturing site was analysed gravimetrically for its lead content.

A 2000 mL sample was treated with sodium sulfate solution until no further precipitate was observed to form. After filtering and drying to constant weight, 1.214 g of lead sulfate was obtained.

Calculate the level of lead ions in the groundwater in mg L⁻¹.
Solution: In cases such as this, an ionic equation is more practical than a full equation. This is because we are interested in the Pb\(^{2+}\) ions only. We can therefore write:

\[
Pb^{2+}(aq) + SO_4(aq) \rightarrow PbSO_4(s)
\]

\[n(PbSO_4) = 1.21 \text{ g}
\]

\[M(PbSO_4) = 303.3 \text{ g mol}^{-1}
\]

Therefore, \[n(PbSO_4) = \frac{1.21}{303.3} = 0.00399 \text{ mol}
\]

\[n(Pb^{2+}) : n(PbSO_4) = 1 : 1
\]

Therefore, \[n(Pb^{2+}) = 0.00399 \text{ mol}
\]

Therefore, \[m(Pb^{2+}) = 0.00399 \times 207.2 = 0.827 \text{ g}
\]

Since the amount analysed was 2000 mL (2 L), the concentration of Pb\(^{2+}\) equals:

\[\frac{0.827}{2} = 0.414 \text{ g L}^{-1}
\]

\[= 414 \text{ mg L}^{-1}
\]

Alternative solution:

This relies on the assumption that all the lead in the original sample precipitates. Of course, this should be true of any properly designed gravimetric process!

When the molar mass of PbSO\(_4\) is evaluated, it becomes clear that, in the 303.3 g that represents 1 mole, 207.2 g is due to lead.

The fraction of lead in PbSO\(_4\) is therefore \[\frac{207.2}{303.3}
\]

It follows that in 1.214 g of PbSO\(_4\) there are \[\frac{207.2}{303.3} \times 1.21 = 0.827 \text{ g}
\]

of lead.

The rest of the calculation is the same as above.

Sample problem 15.10

The zinc content in a water sample was analysed as follows.

A 1000 mL sample was treated with a solution of ammonium hydrogen phosphate, (NH\(_4\))\(_2\)HPO\(_4\), to precipitate all the zinc ions present. A precipitate of NH\(_4\)ZnPO\(_4\) was obtained, which was then decomposed by heating to produce 2.918 g of Zn\(_2\)P\(_2\)O\(_7\).

Calculate the concentration of zinc in the sample in g L\(^{-1}\).

Solution: This appears to be much more complicated but is easily solved using the alternative method in sample problem 15.9. We assume that, no matter how many steps are involved, all the zinc in the original sample ends up in the final precipitate, Zn\(_2\)P\(_2\)O\(_7\), that is weighed.

\[M(Zn_2P_2O_7) = 304.8 \text{ g mol}^{-1}
\]

of which 130.8 g is zinc.

Therefore, fraction of zinc in Zn\(_2\)P\(_2\)O\(_7\) = \[\frac{130.8}{304.8}
\]

Therefore, \[m(Zn) = \frac{130.8}{304.8} \times 2.918 \text{ g}
\]

\[= 1.252 \text{ g}
\]

As this is already in 1 L, the concentration of zinc = 1.252 g L\(^{-1}\).
**Revision question**

16. The calcium content of a sample can be determined gravimetrically by first precipitating the calcium ions present as calcium oxalate. When this precipitate is heated, it decomposes completely to produce calcium oxide. In testing the purity of a calcium chloride sample, a chemist used gravimetric analysis and obtained 8.81 g of calcium oxide from an original 18.0 g sample of calcium chloride. Calculate the percentage purity of the calcium chloride.

**Examining sources of error**

Although most gravimetric procedures have a clearly recognisable series of steps, the properties of the chemicals involved may necessitate some modifications to the method in particular circumstances. A thorough appreciation of the method is also important in evaluating the limits of your results. If certain things happen during the analysis, it is important to predict how these may affect the final result. Table 15.5 shows some possible sources of error.

**TABLE 15.5 Sources of error**

<table>
<thead>
<tr>
<th>Action</th>
<th>Effect on analysis result</th>
<th>Reason</th>
</tr>
</thead>
<tbody>
<tr>
<td>insoluble materials not filtered out before forming the precipitate</td>
<td>overestimated</td>
<td>The apparent mass of the precipitate will increase.</td>
</tr>
<tr>
<td>not enough of the precipitate-forming chemical added</td>
<td>underestimated</td>
<td>Not enough of the precipitate will form as some of the ions that are being analysed will remain in solution.</td>
</tr>
<tr>
<td>forming a precipitate that is too soluble</td>
<td>underestimated</td>
<td>Not all of the ions being analysed will be in the precipitate.</td>
</tr>
<tr>
<td>forming extra precipitate due to the presence of other competing ions</td>
<td>overestimation</td>
<td>Too much of the precipitate will form.</td>
</tr>
<tr>
<td>weighing the precipitate before it is dry</td>
<td>overestimation</td>
<td>The water present will increase the apparent mass of the precipitate.</td>
</tr>
<tr>
<td>not rinsing the precipitate before drying it</td>
<td>overestimation</td>
<td>As the precipitate dries, other soluble chemicals will begin to crystallise out of the small amount of solution still trapped in the precipitate. These will add to the mass.*</td>
</tr>
<tr>
<td>adding too much of the precipitate-causing chemical</td>
<td>no effect</td>
<td>This is a necessary part of the method to make sure that all of the required ions are in the precipitate. The chemical must be in excess.</td>
</tr>
<tr>
<td>using too much water for the initial dissolving</td>
<td>no effect</td>
<td>This is a practical consideration — the more water you have, the longer the filtering step.</td>
</tr>
</tbody>
</table>

*Note: To avoid this situation, the precipitate should always be washed with a small amount of pure solvent before it is dried and weighed. Too much water or solvent could cause some of the precipitate to redissolve. In this case, the final result will be underestimated.
Chapter review

Summary

- Chemical analysis is the process of determining the substances present in a test sample. A range of techniques exist for doing this.
- The choice of a particular technique depends on many factors, the most important of which are the properties of the substance that is being tested for.
- Qualitative analysis is the process of determining which substances are present in a sample.
- Quantitative analysis is the process of determining how much of a substance is present.
- Strict protocols must be observed when collecting water samples for analysis so that the results obtained are accurate.
- The salts dissolved in water samples come from a variety of sources, including natural sources as well as the result of human activity. They include a range of salts as well as heavy metal compounds and organo-metallic substances.
- A contaminant is a substance that makes water unsuitable for an intended use.
- Contaminants enter waterways through a variety of methods including direct discharge, stormwater run-off, contaminated air contact and contact with contaminated groundwater.
- Stoichiometry is the study of the relative amounts — ratios — of substances involved in chemical reactions. This chapter introduced:
  - mass–mass stoichiometry
  - mass–concentration stoichiometry.
- The coefficients in a balanced chemical equation tell us the relative numbers of moles of reactants and products and can be used to find the mole ratio of one substance to another.
- A four-step approach may be used to solve stoichiometric problems.
  
  Step 1: Write a balanced chemical equation for the reaction, identifying the known (given) and unknown (required) quantities of substance.
  
  Step 2: Calculate the number of moles of the known quantity of substance.
  
  Step 3: From the equation, find the mole ratio that states the proportion of known to unknown quantities in the reaction and use it to calculate the number of moles of the required substance.
  
  Step 4: Calculate the required quantity of the substance.
- Whenever two or more reactants are given in a chemical reaction, the limiting reactant must be identified before we can calculate the maximum amount of product that may form. A limiting reactant is completely used up in a chemical reaction. The other reactants are known as excess reactants and are not used up.
- Instrumental colorimetry can be used for coloured solutions. It relies on measuring how much light of a complementary colour is absorbed by a solution.
- Atomic absorption spectroscopy (AAS) and UV-visible spectroscopy both rely on the accurate measurement of radiation of a particular frequency.
- AAS is suitable for determining many metals.
- All the instruments mentioned above may be calibrated for quantitative analysis by obtaining readings from a number of standards and then plotting a calibration curve.
- The choice of instrument for a particular analysis depends on the properties of the material that is under analysis.
- Gravimetric analysis is analysis by mass.
- A simple method of determining moisture content is to gently heat a sample and record the mass lost as the water is driven off.
- A more sophisticated version involves the formation of suitable precipitates, the amounts of which are stoichiometrically related to the amount of the component being analysed.
- This method involves weighing the sample to be analysed, dissolving the sample, forming the required precipitate, filtering the precipitate, and weighing the precipitate to constant mass.
- The exact details of a given method depend on the properties of the substances involved.
- If the properties of the substances are not carefully considered, or if mistakes are made, the final result will be affected. It is important to be able to predict how such situations will affect the final calculated result.

Multiple choice questions

1. Which of the following would be most likely to be a contaminant in a sample of surface water?
   
   A. \( \text{Cl}^- \)  
   B. \( \text{SO}_4^{2-} \)  
   C. \( \text{Ca}^{2+} \)  
   D. \( \text{Hg}^+ \)

2. Which of the following is an organometallic substance?
   
   A. methyl chloride  
   B. methylzinc  
   C. lead nitrate  
   D. carbon dioxide
3. A field technician collected a creek water sample (CW) and added two preserving agents (A and B) to his sample. In his field kit was also a container of deionised water (DW).

   The protocol also called for the preparation of a blank.

   The substances that the blank should contain are:
   A  A, B and CW
   B  A, B and DW
   C  A, B
   D  DW only.

4. A calibration curve is a graph of instrumental reading against:
   A  mass
   B  time
   C  volume
   D  concentration.

5. A standard used in instrumental analysis is:
   A  a solution containing the sample being tested
   B  a solution of exactly 10.00 ppm
   C  a solution of exactly known concentration
   D  a list of prescribed tolerances for use of the instrument.

6. Magnesium reacts with oxygen according to the equation:

   \[ 2\text{Mg}(s) + \text{O}_2(g) \rightarrow 2\text{MgO}(s) \]

   In this reaction:
   A  2 g of magnesium react with 1 g of oxygen to produce 2 g of magnesium oxide
   B  2 g of magnesium react with exactly 1 g of oxygen
   C  2 moles of magnesium are needed for every mole of oxygen used
   D  2 moles of oxygen are needed for every mole of magnesium used.

7. Before digital printing, sodium thiosulfate, \( \text{Na}_2\text{S}_2\text{O}_3 \), known as ‘hypo’ by photographers, was used to remove excess silver bromide, \( \text{AgBr} \), in the liquid-based film-developing process according to the equation:

   \[ 2\text{Na}_2\text{S}_2\text{O}_3(aq) + \text{AgBr}(s) \rightarrow \text{Na}_3\text{Ag(S}_2\text{O}_3)_2(aq) + \text{NaBr}(aq) \]

   In the balanced equation for the reaction between sodium thiosulfate and silver bromide:
   A  1 mole of sodium thiosulfate solution produces 1 mole of sodium bromide solution
   B  3 moles of sodium thiosulfate solution produce 2 moles of \( \text{Na}_3\text{Ag(S}_2\text{O}_3)_2 \)
   C  1 mole of sodium thiosulfate solution produces 2 moles of sodium bromide solution
   D  1 mole of silver bromide produces 1 mole of \( \text{Na}_3\text{Ag(S}_2\text{O}_3)_2 \).

8. Phosphorus may be prepared from calcium phosphate according to the equation:

   \[ 2\text{Ca}_3(\text{PO}_4)_2(s) + 6\text{SiO}_2(s) + 10\text{C}(s) \rightarrow \text{P}_4(s) + 10\text{CO}(g) + 6\text{CaSiO}_3(s) \]

   How much phosphorus can be produced if 1000 kg of calcium phosphate is used completely?
   A  50 kg
   B  100 kg
   C  200 kg
   D  400 kg

9. The fertiliser diammonium phosphate (DAP) is a popular source of phosphate fertiliser for farmers. It is produced by the reaction of ammonia with phosphoric acid according to:

   \[ 2\text{NH}_3(g) + \text{H}_3\text{PO}_4(aq) \rightarrow (\text{NH}_4)_2\text{HPO}_4(aq) \]

   The mass of fertiliser that would be produced by the complete reaction of 100 kg ammonia in this process would be:
   A  5.88 kg
   B  388 kg
   C  776 kg
   D  1553 kg.

10. A gelatinous precipitate of iron(III) hydroxide may be prepared according to the equation:

    \[ \text{FeCl}_3(aq) + 3\text{NaOH}(aq) \rightarrow 3\text{NaCl}(aq) + \text{Fe(OH)}_3(s) \]

    A solution containing 16.23 g of \( \text{FeCl}_3 \) is mixed with 300 mL of a 1.00 M \( \text{NaOH} \) solution.
    Which of the following statements is correct?
    A  \( \text{FeCl}_3 \) is in excess.
    B  \( \text{NaOH} \) is in excess.
    C  \( \text{FeCl}_3 \) is the limiting reagent.
    D  Neither reagent is in excess.

11. We want to analyse a sample of salty water for its chloride ion content. This is to be done using gravimetric analysis. Which of the following chemicals could be added for the formation of a precipitate?
    A  \( \text{CaCO}_3 \)
    B  \( \text{Ba(NO}_3)_2 \)
    C  \( \text{K}_2\text{SO}_4 \)
    D  \( \text{AgNO}_3 \)

12. The heating and drying of a precipitate to constant weight ensures that:
    A  there is no water left in it
    B  impurities are removed from it
    C  trace amounts left in solution are precipitated
    D  absorption of gases from the atmosphere is minimised.

13. A sample of lawn food is analysed gravimetrically. As part of the procedure, a precipitate of barium sulfate is formed. However, when this is later weighed, it is still slightly damp. As a result of this, the calculated percentage of sulfate would:
    A  be increased
    B  be decreased
    C  be unchanged
    D  vary in a random manner.
14. An atomic absorption spectrometer was used to determine the amount of iron lost by peas in the cooking process. Using a suitable means of extraction, the iron was first extracted from a 5.0 g sample of uncooked peas to produce 100 mL of extract. When tested in the instrument, the uncooked peas gave an absorbance reading of 0.20. The AAS was then calibrated and its calibration curve is shown below.

The mass of iron (in mg) in the original sample of uncooked peas is:

A  0.21  
B  0.25  
C  2.1  
D  2.5

15. Using the technique of AAS, we want to accurately determine the concentration of some copper(II) sulfate solution. The concentration of this solution is known to be about 0.02 M. A set of standards is available, the concentrations of which range from 2 to 16 mg (of copper) per litre.

By what factor should the copper(II) sulfate solution be diluted prior to being drawn into the instrument?

A  1  
B  10  
C  100  
D  1000

Review questions

General analysis

1. Classify the following analyses as either qualitative or quantitative.

(a) Analysis of the propellant from a spray can by an instrument, to check the claim that it does not contain chlorofluorocarbons, CFCs

(b) Adding a piece of ‘testape’ to a diabetic’s urine to estimate the glucose level present

(c) Instrumental checking of the level of mercury in a sample of fish

(d) Analysis of a hair-colouring preparation ‘containing less than 1.5% aromatic nitroamines’, to check the claim

2. A number of qualitative tests are used to identify various substances. Find out the tests that are used to identify the following.

(a) Carbon dioxide gas
(b) Starch
(c) Oxygen gas
(d) Protein in a food sample
(e) Hydrogen gas
(f) Water

Water solutes and sampling

3. (a) Define the term ‘contaminant’.

(b) Give an example of a situation in which water might be unsuitable for one particular use but suitable for another use.

(c) Discuss your answer to part (a) in light of your answer to part (b)

4. Methylmercury can be a serious contaminant in water because it accumulates in fish and shellfish, which can subsequently be eaten by people.

Research and answer the following questions about methylmercury using the internet or other suitable references.

(a) What do the terms ‘inorganic mercury’ and ‘organic mercury’ mean?

(b) Describe how methylmercury may be produced in the environment.

(c) What is Minamata disease? Where did this first occur and what was its cause?

(d) Where have other outbreaks of this disease occurred and what were their causes?

(e) Do any other metals form compounds similar to methylmercury?

5. Procedures to be followed for the collection of water samples are listed in the document Sampling and analysis of waters, wastewaters, soils and wastes. See the Sampling and analysis weblink in the Resources section of your eBookPLUS to access this document. Use appendix A of the document to list some of the procedures that need to be followed to collect water samples for testing the following.

(a) sulfate

(b) magnesium ions

(c) cyanide

(d) Fe$^{2+}$

(e) total mercury

(f) pH
Stoichiometry

6. A solution containing 5.10 g of barium nitrate reacts completely with a solution of sodium sulfate. The unbalanced equation for this reaction is:

\[ \text{Ba(NO}_3\text{)}_2(aq) + \text{Na}_2\text{SO}_4(aq) \rightarrow \text{NaNO}_3(aq) + \text{BaSO}_4(s) \]

(a) Balance the equation above by inserting the necessary coefficients and identify the precipitate formed.
(b) Calculate the mass of precipitate formed.

Mass–mass stoichiometry

7. Nitrogen in the cylinder of a car reacts with oxygen to produce the pollutant nitrogen monoxide.

\[ \text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g) \]

(a) How many moles of nitrogen are needed to produce 1.52 mol nitrogen monoxide?
(b) How many grams of oxygen are needed for this reaction?

8. Barbecues burning charcoal briquettes are unsafe for indoor use because of the colourless, odourless, poisonous gas produced.

(a) Find the \(n(\text{O}_2)\) gas that reacts with 3.5 g of charcoal briquettes (assume pure C) to produce carbon monoxide.
(b) If there is a plentiful supply of air, a safe colourless, odourless gas is produced. Find the mass of this gas produced if the same amount of charcoal is burned. You will need to write another equation.

9. When sodium and chlorine are reacted, table salt is produced.

(a) Write the balanced equation for the reaction.
(b) If 10.0 g of sodium is used, how much table salt would be produced?

10. In respiration, the equation for the reaction that produces energy in our bodies is:

\[ \text{C}_{6}\text{H}_{12}\text{O}_6(aq) + 6\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \]

If 8.90 g of glucose is used, determine:
(a) the mass of oxygen needed
(b) the mass of carbon dioxide produced.

11. The silver used in jewellery and tableware becomes tarnished when exposed to air containing small amounts of hydrogen sulfide. The tarnish is a layer of silver sulfide.

\[ 4\text{Ag}(s) + 2\text{H}_2\text{S}(g) + \text{O}_2(g) \rightarrow 2\text{Ag}_2\text{S}(s) + 2\text{H}_2\text{O}(g) \]

Calculate the mass of the tarnish when 0.025 g of silver is reacted.

12. In the final step of the Contact Process, where sulfuric acid is manufactured industrially, controlled addition of water to oleum, \(H_2S_2O_7\), produces pure sulfuric acid. The equation for the reaction is:

\[ \text{H}_2\text{S}_2\text{O}_7(l) + \text{H}_2\text{O}(l) \rightarrow 2\text{H}_2\text{SO}_4(l) \]

Calculate the mass of sulfuric acid produced when 5.00 kg of oleum is dissolved in water.

13. The metal tungsten, used to make the filaments for incandescent light bulbs, can be obtained from its oxide by reduction with hydrogen.

\[ \text{WO}_3(s) + 3\text{H}_2(g) \rightarrow \text{W}(s) + 3\text{H}_2\text{O}(g) \]

(a) What mass of tungsten can be obtained from 200 g of its oxide?
(b) What mass of hydrogen is required?

14. In a class experiment, a strip of copper was placed in an aqueous solution of silver nitrate.

Initial mass of copper strip = 4.36 g
Final mass of copper strip = 2.21 g

(a) Write an equation for the reaction.
(b) What mass of silver formed in the reaction?

15. A 1.50 g sample of paint pigment was dissolved in an aqueous solution of silver nitrate. The precipitate had a mass of 0.0806 g. Find the percentage of lead by mass in the pigment.

16. Aluminium burns in oxygen to produce an intense burst of light. Aluminium oxide is produced in the process. The equation for the reaction is:

\[ 4\text{Al}(s) + 3\text{O}_2(g) \rightarrow 2\text{Al}_2\text{O}_3(s) \]

Calculate the mass of aluminium oxide produced from 5.0 g of aluminium.

17. As an emergency procedure, the Apollo 13 astronauts used lithium hydroxide to remove carbon dioxide from the interior of their crippled spacecraft as it returned from the moon. Like all hydroxides, lithium hydroxide forms the appropriate metal carbonate when it reacts with carbon dioxide.

The equation for this reaction is:

\[ 2\text{LiOH}(s) + \text{CO}_2(g) \rightarrow \text{Li}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \]

(a) Calculate the mass of carbon dioxide that could be removed per kilogram of lithium hydroxide.
(b) Write the equation for the reaction between lithium hydroxide and carbon dioxide.
(c) From part (b), calculate the mass of carbon dioxide that can be removed per kilogram of sodium hydroxide.
(d) Use your answers to parts (a) and (c) to suggest a reason for the choice of lithium hydroxide.
Hydroxide rather than sodium hydroxide in a spacecraft.

(e) Derive the ionic equations for both the reactions mentioned in this question.

18. Limestone is an important raw material for industry. When heated in a kiln, it decomposes to form quicklime, CaO, and carbon dioxide. A typical kiln is shown in the figure below.

The equation for this reaction is:

\[ \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \]

(a) If limestone containing 83.5% calcium carbonate is used, calculate the mass of quicklime that would be produced from 100 tonnes of this limestone.

(b) This process is sometimes called ‘lime burning’. Why is this not a correct term to use?

Mass–concentration stoichiometry

19. What volume of 1.3 M HCl just neutralises 2.5 g of Ca(OH)\(_2\)?

\[ \text{Ca(OH)}_2(s) + 2\text{HCl(aq)} \rightarrow \text{CaCl}_2(\text{aq}) + 2\text{H}_2\text{O(l)} \]

20. What mass of copper is required to react completely with 250 mL of 0.100 M AgNO\(_3\)?

\[ \text{Cu(s)} + 2\text{AgNO}_3(\text{aq}) \rightarrow \text{Cu(NO}_3)_2(\text{aq}) + 2\text{Ag(s)} \]

Analysing with instruments

21. Examine the graph on page 310.

(a) Explain why electrical conductivity can be used to measure the level of salt in the river.

(b) Describe the trends in salt content before the early 1980s and after the early 1980s.

(c) Why is it incorrect to interpret these results as evidence of sodium chloride content?

(d) Why is it more correct to interpret the results in terms of total salt content?

22. An atomic absorption spectrometer was used to check the iron content of a brand of commercially available soda water. To calibrate the instrument, four samples of known concentrations were used. The sample of soda water was then analysed. The following results were obtained (absorbance being measured in appropriate units):

<table>
<thead>
<tr>
<th>Standard 1</th>
<th>Absorbance 0.053</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration 1.00 ppm</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard 2</th>
<th>Absorbance 0.109</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration 2.00 ppm</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard 3</th>
<th>Absorbance 0.157</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration 3.00 ppm</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard 4</th>
<th>Absorbance 0.266</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration 5.00 ppm</td>
<td></td>
</tr>
</tbody>
</table>

Sample: 

(a) For a concentration of 0.00 ppm, what should be the value of the absorbance?

(b) Plot the calibration curve from the data above.

(c) Hence, estimate the concentration of iron in the soda water.

(d) Suggest a way in which a computer might replace part (b).

23. Flame emission spectroscopy is similar to atomic absorption spectroscopy, except that ‘transmittance’ is measured rather than ‘absorbance’. Sodium levels in mineral waters were analysed by flame emission spectroscopy.

Sodium produces an orange light, with one of the wavelengths present being 589 nanometres (589 \times 10^{-9} \text{ metres}). The detector of the instrument was therefore set to measure the intensity of the emitted light at this wavelength.

Sample standards were run first, followed by two brands of mineral water. The results are shown in the table below.

<table>
<thead>
<tr>
<th>Sodium (mg L(^{-1}))</th>
<th>% transmittance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>22</td>
</tr>
<tr>
<td>20</td>
<td>44</td>
</tr>
<tr>
<td>30</td>
<td>66</td>
</tr>
<tr>
<td>40</td>
<td>85</td>
</tr>
<tr>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Sample 1 (Australian)</td>
<td>86</td>
</tr>
<tr>
<td>Sample 2 (French)</td>
<td>12</td>
</tr>
</tbody>
</table>

Results from analysis of sodium levels in mineral water
(a) Plot a calibration curve using the sodium standards.
(b) From this curve, deduce the sodium levels in each of the samples analysed.

24. The level of mercury in various waterways can have serious implications for human health if foods such as oysters or flake produced in such waters are consumed. Consequently, various agencies regularly measure mercury levels in such waterways and in food samples produced from them.

In one particular analysis, a sample of water was analysed in an instrument and gave a reading of 0.375.

Without altering the setting of the instrument, standard samples containing known levels of mercury were then analysed, giving the results shown in the table below.

Results from analysis of water sample containing mercury

<table>
<thead>
<tr>
<th>Concentration of mercury sample (mg L⁻¹)</th>
<th>Reading</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.102</td>
</tr>
<tr>
<td>4</td>
<td>0.205</td>
</tr>
<tr>
<td>6</td>
<td>0.307</td>
</tr>
<tr>
<td>8</td>
<td>0.410</td>
</tr>
<tr>
<td>10</td>
<td>0.512</td>
</tr>
</tbody>
</table>

(a) What is the concentration of phosphorus in the diluted solution?
(b) What is the percentage by mass of phosphorus in the detergent?
(c) What colour do you think the light used for this analysis would be?

25. The level of phosphorus (as phosphate) in a detergent may be determined colorimetrically by reacting it with a molybdate solution to develop an intense blue compound.

In the analysis of one particular brand of detergent, a 1.000 g sample was dissolved in 1000 mL. A carefully measured 20.0 mL sample of this was then treated with molybdate solution and heated to develop the blue colour.

When analysed in an instrumental colorimeter, a reading of 0.260 was obtained.

Four standard solutions containing phosphorus levels of 5, 10, 15 and 20 ppm were similarly treated and their absorbances measured to produce the graph shown above right.

(a) What is the concentration of phosphorus in the detergent?
(b) What is the percentage by mass of phosphorus in the detergent?
(c) What colour do you think the light used for this analysis would be?

26. In each of the following reactions, a precipitate is formed. Write the full balanced equation for each reaction and then write the corresponding ionic equation. (The precipitate formed in each case is shown in brackets.)

(a) Silver nitrate solution is added to sodium chloride solution. (silver chloride)
(b) Barium chloride solution is added to sodium sulfate solution. (barium sulfate)
(c) Lead nitrate solution is added to potassium chromate solution. (lead chromate)
(d) Sodium phosphate solution is added to silver nitrate solution. (silver phosphate)
(e) Dilute hydrochloric acid is added to lead nitrate solution. (lead chloride)

27. State whether the following substances are soluble or insoluble in water.

(a) sodium carbonate
(b) calcium carbonate
(c) barium sulfate
(d) silver chloride
(e) ammonium phosphate
(f) silver nitrate

28. The moisture content of an area of soil is one of its most important properties. A simple method for determining this is to take a soil sample and heat it in an oven at 105 °C until constant mass is achieved.
In a particular experiment, the following results were obtained.
Initial mass 124.829 g
Mass (after 60 min) 115.813 g
Mass (after 70 min) 109.614 g
Mass (after 80 min) 107.214 g
Mass (after 90 min) 107.212 g
Mass (after 100 min) 107.214 g

(a) Calculate the percentage of moisture in the soil sample.
(b) Why is the sample heated until constant mass is obtained?
(c) In a situation such as this, why would it be unwise to rely on the results from a single sample?

To determine the percentage of arsenic in a particular brand of pesticide, a 2.15 g sample is treated to precipitate all the arsenic as its sulfide, As₂S₃. If 0.353 g of precipitate is obtained, calculate the percentage of arsenic in the pesticide.

To test the percentage of sodium chloride in a sample of rock salt, a carefully weighed mass (0.997 g) was first dissolved in water. Silver nitrate solution was then added until no further precipitate was observed to be forming. This precipitate was filtered using a filtering crucible and then dried in an oven to constant weight. The mass of precipitate obtained was 2.359 g.

(a) What is the name of the precipitate formed in this process?
(b) Calculate the percentage of sodium chloride in the rock salt, assuming that it is the only source of chloride ions.

Sulfur in azalea fertiliser is present in the form of soluble sulfates. To check the percentage of sulfur in such a product, a 2.322 g sample was weighed and dissolved in water. Barium chloride was then added under carefully controlled conditions to precipitate all the sulfate present as barium sulfate. After filtering, washing with water and drying, the mass of precipitate obtained was 0.564 g.

(a) Calculate the mass of sulfur in the precipitate and hence the percentage of sulfur in the sample as analysed.
(b) What is the effect on the final result if the precipitate is not washed with water before drying?

**Experimental procedures and design**

In each of the following situations, we want to analyse gravimetrically the component written in bold type. From the list in brackets, choose the ions that should be added to achieve this.
(a) sulfamate (magnesium, aluminium, lead, ammonium)
(b) chloride (sodium, barium, calcium, silver)
(c) carbonate (potassium, lithium, barium, ammonium)
(d) iron(III) (nitrate, acetate, sulfate, hydroxide)

33. In gravimetric analysis, why are precipitates dried to constant weight?
34. ‘Every compound is soluble to a greater or lesser extent.’ Discuss the implications of this statement for gravimetric procedures. Would the above lead to a systematic or a random error? Explain.
35. Salinity is a serious problem in many of Victoria’s irrigation areas. Design and describe an experiment whereby the level of salt in a water sample can be determined gravimetrically.
36. The following steps were considered by a student when designing a gravimetric procedure to estimate the level of magnesium carbonate in a sample of epsom salts. The steps have been written down in random order. Rearrange these steps into an order that would be acceptable, remembering that some steps might be repeated more than once and that some steps might not be required.
(a) Filter and collect the precipitate produced.
(b) Add a solution of potassium chloride.
(c) Accurately weigh out a sample of epsom salts.
(d) Accurately weigh the precipitate.
(e) Dissolve the epsom salts in a volume of water.
(f) Dry the precipitate.
(g) Measure out an accurate volume of water.
(h) Add a solution of barium chloride.
37. In a particular gravimetric procedure, a sample was weighed. It was then dissolved in water and the component of interest precipitated by adding a suitable chemical. This precipitate was then filtered and washed with a small quantity of water. Finally, it was dried in an oven before being weighed. The percentage (by mass) of the component was then calculated. Below are listed some possible faults that might occur in an analysis of this type. For each fault, predict the effect it would have on the final result.
(a) The precipitate is not dried completely before the final weighing.
(b) The precipitate is dried before it is washed with a quantity of water.
(c) The original sample is dissolved in an excessive volume of water.
(d) The experiment is performed at too high a temperature.
Exam practice questions

In a chemistry examination you will be required to write a number of short and extended response questions.

Extended response questions

1. A sample of limestone is analysed for its calcium carbonate content as follows.
   A 25.00 g sample is crushed and heated to a high temperature. It is then cooled, weighed and reheated until a constant mass is obtained. The mass remaining at the end of this process is 11.64 g.
   (a) What gas is evolved during this process?
   (b) Write the equation for the decomposition of calcium carbonate in the limestone at high temperature.
   (c) Use the results obtained to calculate the mass of calcium carbonate in the limestone, and hence its percentage purity.
   (d) State one important assumption in this method. 6 marks

2. Phosphorus is an important plant nutrient and is therefore present in many fertilisers.
   It can be determined gravimetrically by carrying out a number of steps, eventually leading to its precipitation as insoluble Mg₃P₂O₇. In one such analysis, a 14.298 g sample of fertiliser yielded 4.107 g of Mg₃P₂O₇ precipitate.
   (a) Calculate the mass of phosphorus in the precipitate.
   (b) Hence, calculate the percentage of phosphorus in the fertiliser.
   (c) State one important assumption that is made in this method. 4 marks

3. As part of a research project into tidal effects in a river estuary, a student takes water samples at various locations and determines the concentration of salt (as sodium chloride) in each. Her method involves collecting 10.0 L of water from each location and boiling it to reduce the volume. Excess silver nitrate solution is then added to precipitate all the chloride ions present as silver chloride. This precipitate is then collected, dried and weighed to constant mass.
   Following this procedure, one particular sample produced 4.463 g of precipitate.
   (a) Write a balanced equation for the reaction that leads to the formation of the precipitate.
   (b) Calculate the mass of sodium chloride in this particular sample.
   (c) Hence, calculate the concentration of sodium chloride in this sample, in g L⁻¹.
   (d) In what way does boiling the sample to reduce its volume affect your calculation?
   (e) Some important assumptions are made by the student in this procedure. Name one. 7 marks