

# Chapter

# MONITORING AND MANAGING WATER QUALITY

# 14



**Figure 14.1**

This photo shows a beautiful mountain stream cascading between moss covered rocks. The water looks good enough to drink; but is it safe? An environmental chemist can test the water to determine its purity.

## Introduction

Water is a vital part of our daily lives. More than 65% of our body is composed of water, and unless we consume water daily through eating and drinking, our bodies cannot function and death will result. High quality, potable water is produced from water that is collected in our catchments and dams. This water must undergo many purification steps before it is suitable for human consumption. Analytical chemists are employed to manage and monitor the water purification process.

## In this chapter

- |                                |          |
|--------------------------------|----------|
| 14.1 Testing for water quality | page 318 |
| 14.2 Water purification        | page 338 |

# 14.1 TESTING FOR WATER QUALITY

## Remember

Before beginning this section, you should be able to:

- identify the importance of water as a solvent
- explain why different measurements of concentration are important
- describe the use of the pH scale in comparing acids and bases
- identify pH as  $-\log_{10} [H^+]$  and explain that a change in pH of 1 means a tenfold change in  $[H^+]$ .

## Key content

By the end of this section, you should be able to:

- identify that water quality can be determined by considering:  
(a) concentrations of common ions  
(b) total dissolved solids  
(c) hardness  
(d) turbidity  
(e) acidity  
(f) dissolved oxygen and biochemical oxygen demand
- identify factors that affect the concentrations of a range of ions in solution in natural bodies of water such as rivers and oceans
- perform first-hand investigations to use qualitative and quantitative tests to analyse and compare the quality of water samples
- gather, process and present information on the range and chemistry of the tests used to (a) identify heavy metal pollution of water and (b) monitor possible eutrophication of waterways.

**qualitative tests:** investigations used to identify the presence or absence of elements, ions or molecules in a sample

**quantitative tests:** investigations used to determine the amount of a given element or compound in a known weight or volume of material

## Water quality tests

Analytical and environmental chemists carry out a variety of **qualitative** and **quantitative tests** to determine the quality of water in our rivers and dams.

## Testing for common ions

The concentration of ions in sea water is high compared with their concentration in fresh river water. Table 14.1 compares the concentrations of some of these common ions in sea water, in which sodium and chloride ions are the most abundant.

**Table 14.1** Typical ion concentrations in sea water

Ion	Concentration in sea water (ppm)
chloride	19 000
sulfate	2 650
carbonate/hydrogen carbonate	140
sodium	10 550
magnesium	1 300
calcium	400
potassium	390



**Figure 14.2**

Analytical chemists test water quality to determine if water is suitable for drinking, or to determine if irrigation water is suitable for particular crops.

**Table 14.2** Global average ion concentrations in fresh water

<b>Ion</b>	<b>Concentration in fresh water (ppm)</b>
chloride	5.7
sulfate	6.6
carbonate/hydrogen carbonate	52
sodium	5.3
magnesium	3.6
calcium	13.2
potassium	1.2

**potable water:** water that is fit to drink

Crops vary in their tolerance of salt in the irrigation water. Citrus trees will not grow well if the salt levels in the irrigation water are greater than 500 ppm. Apples and pears, however, grow well in water with salt levels between 500–1500 ppm.

**Potable water** must have low ion concentrations, otherwise the water will taste slightly salty. Table 14.3 shows the concentrations of some common ions in the Sydney water supply. These concentrations are well below the guidelines established by the National Health and Medical Research Council (NHMRC).

**Table 14.3** Ions in the Sydney water supply

<b>Ion</b>	<b>Concentration (ppm)</b>	<b>NHMRC recommended maximum concentration of ions (ppm)</b>
chloride	20	400
sulfate	8	400
nitrate	0.4	10
fluoride	1	1.7
sodium	10	300
calcium	9	200
aluminium	0.2	0.2

Traditionally, the concentration of ions in natural waters was determined by ‘wet’ methods. These wet procedures involved gravimetric or volumetric analysis and were very time consuming, especially if the ions were in low concentrations. In more modern times, most water analysis is performed using instrumental methods. Instrumental methods are usually more accurate than the older methods. These instrumental methods include the use of ion-selective electrodes, chromatography and atomic absorption spectrometry.

### Examples: Qualitative tests

Two important examples of **qualitative tests** are the testing of sulfate and chloride ions.

#### Testing for sulfate ions

The sample of water is first acidified with a little nitric acid to remove any carbonate or hydrogen carbonate ions that could be present. Drops of barium nitrate solution are added and a white precipitate ( $\text{BaSO}_4$ ) suggests the presence of sulfate ions. Any phosphate ions present will not precipitate in acidic solution.

#### Testing for chloride ions

The acidified water sample is tested with silver nitrate solution. The appearance of a white precipitate ( $\text{AgCl}$ ) suggests the presence of chloride ions.

**qualitative test:** investigation used to identify the presence or absence of elements, ions or molecules in a sample

## Examples: Quantitative tests

**quantitative tests:** investigations used to determine the amount of a given element or compound in a known weight or volume of material

Two important examples of **quantitative tests** are the gravimetric analysis of chloride ions and the ion-selective electrode-testing for fluoride ions.

### Gravimetric analysis for chloride ions

The chloride ions in fresh water can come from a variety of sources, including natural soil minerals and water runoff from farms. In a tidal river some chloride ions come from the sea. If the chloride level is above 200 ppm, the water can have a slightly salty taste.

A traditional wet method for determining chloride ions in water is to precipitate the chloride ions from a known volume of water as insoluble silver chloride and then weigh the dried precipitate. If the concentration of chloride is low in the water sample, it may need to be initially concentrated by evaporation prior to analysis.

### SAMPLE PROBLEM 14.1

### SOLUTION

A 5.0-litre (5.0 kg) sample of river water was collected. After acidification with nitric acid, sufficient silver nitrate was added to precipitate the chloride ions as silver chloride. The silver chloride was collected, washed, dried and weighed. The mass of silver chloride was 0.235 g. Calculate the chloride ion concentration in parts per million in the river water.

**Step 1.** Write and interpret the ionic equation for this precipitation.

The balanced equation is:



The balanced equation shows us that 1 mole (35.45 g) of chloride ions produces 1 mole (143.35 g) of silver chloride.

**Step 2.** Calculate the mass of chloride ions.

The mass,  $m$ , of chloride required to produce 0.235 g of silver chloride is:

$$\begin{aligned}m(\text{Cl}^-) &= 35.45/143.35 \times 0.235 = 0.0581 \text{ g} \\&= 58.1 \text{ mg}\end{aligned}$$

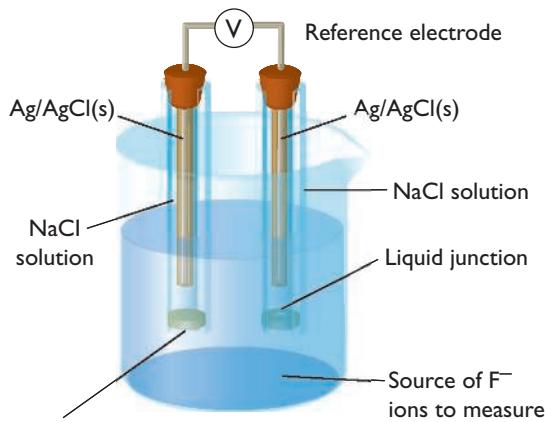
**Step 3.** Calculate the concentration,  $c$ , of chloride ions.

$$\begin{aligned}c(\text{Cl}^-) &= 58.1 \text{ mg}/5.0 \text{ kg} = 11.6 \text{ mg/kg} \\&= 11.6 \text{ ppm}\end{aligned}$$

### Ion-selective electrode testing for fluoride ions

Atomic absorption spectrometry (AAS) can be used to determine the concentration of metal ions, but other methods must be used for anions. One convenient method is to use an ion-selective electrode (ISE). These electrodes can also be used for cation analysis. They have the advantages of size and portability, and thus can be used in field analysis. The ISEs are similar to pH electrodes that are used to measure the hydrogen ion concentration in water. Each ISE is a galvanic cell that has an internal reference electrode (e.g. Ag–AgCl). The voltages measured by these cells are related to concentration using a series of known standards.

An ISE can be used to measure fluoride levels in water. Fluoride is added to Sydney water to help prevent tooth decay, and its levels must be closely monitored. The fluoride ISE is shown in Figure 14.3.



**Figure 14.3**

The concentration of fluoride in water can be rapidly measured using a fluoride ion sensitive electrode.

### SAMPLE PROBLEM 14.2

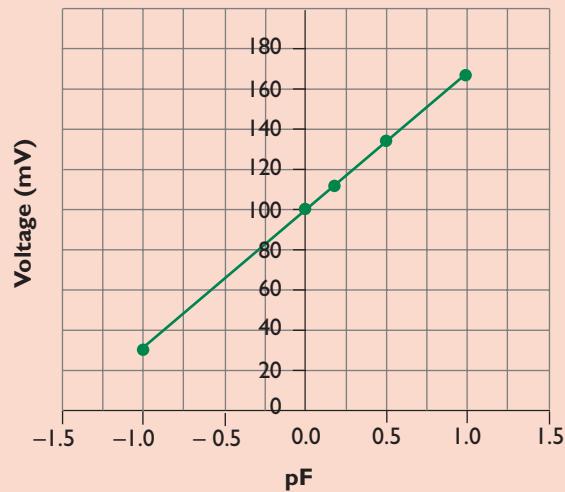
Five standard solutions of fluoride ions were used to calibrate the ISE. The results collected were:

Concentration of fluoride [F <sup>-</sup> ] (ppm)	0.100	1.00	1.60	3.20	10.00
pF = -log [F <sup>-</sup> ]	-1.00	0	0.20	0.51	1.00
Voltage (mV)	31	100	113	135	165

The ISE establishes a linear relationship between pF (negative logarithm of the fluoride ion concentration) and voltage, and then uses this relationship to determine the fluoride concentration of an unknown. A sample of water was tested and the voltage recorded was 80 mV. Use the data to determine the fluoride concentration in the water sample.

### SOLUTION

The following calibration graph (Figure 14.4) is used to determine the fluoride concentration.



**Figure 14.4**

From the graph, the 80 mV is equivalent to a pF of -0.30. Thus, the fluoride ion concentration in the unknown water sample is calculated as follows:

$$\begin{aligned} \text{pF} &= -\log[\text{F}^-] \\ \text{so, } [\text{F}^-] &= 10^{-0.30} \\ &= 0.50 \text{ ppm} \end{aligned}$$

## Testing for total dissolved solids (TDS)

Compared with salt water, freshwater contains less dissolved solids. Most of these dissolved solids are ionic compounds. Smaller amounts of organic molecules are also present. The total amount of dissolved solids fluctuates over time because of the influx of rainwater and floodwater. In Sydney water reservoirs, the typical range of total dissolved solids (TDS) is 40–100 ppm. Artesian bore water has much higher TDS levels (500–1200 ppm). Such bore water is suitable for irrigating some crops (e.g. apples, pears, cabbages and cauliflowers) but other crops (e.g. citrus, carrots, corn and potatoes) are less tolerant and require water with a TDS lower than 500 ppm. TDS values greater than 1000 ppm indicate a degraded waterway. High sodium levels in rivers and lakes are indicative of salinity problems. High potassium levels in fresh water often indicate that leaching of burnt or decaying plant remains has occurred.

Traditional wet methods to measure TDS involve the evaporation of a known volume of water to dryness, and measuring the mass of dry residue left behind. The TDS values are reported in the units of mg/L or ppm.

### SAMPLE PROBLEM 14.3

### SOLUTION

A sample of water from a farm bore was collected and filtered. One litre of the water was slowly evaporated to dryness in a large beaker and the mass of the dry residue determined.

- Explain why the water was filtered before evaporation.
- Use this data to determine the TDS of the water sample.

$$\text{Mass of beaker} = 245.345 \text{ g}$$

$$\text{Mass of beaker + dry residue} = 245.955 \text{ g}$$

- The water was filtered to remove suspended solids.
- Follow these steps.

Step 1. Calculate the mass of residue.

$$\begin{aligned}\text{Mass of residue} &= 245.955 - 245.345 \\ &= 610 \text{ g} \\ &= 610 \text{ mg}\end{aligned}$$

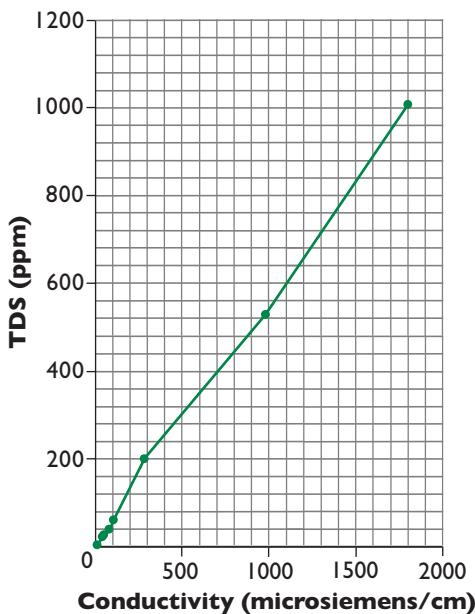
Step 2. Calculate the concentration of the suspended solids in the water.

$$\begin{aligned}\text{TDS} &= 610 \text{ mg/L} \\ &= 610 \text{ ppm}\end{aligned}$$

Modern instrumental methods use a conductivity probe and meter. The conductivity measurement assumes that the great bulk of dissolved solids are ionic and contribute to the total conductivity of the water. This is a reasonable approximation in most analyses. These probes tend to be quite accurate at low ion concentrations but their accuracy drops off as the salinity increases. Conductivity probes are also portable and allow rapid measurement.

The electrodes in a conductivity probe are normally stainless steel rods set a fixed distance apart. Power is supplied from a battery. Most modern meters have automatic temperature adjustment. Electrical conductivity increases by 2% for each degree above 25°C and decreases by 2% for each degree below 25°C. The probe measures conductivity in the units of microsiemens/cm ( $\mu\text{S}/\text{cm}$ ). The probe and meter have to be calibrated

using known standards (e.g. potassium chloride solutions). The graph in figure 14.3 shows the relationship between TDS (measured in ppm) and the electrical conductivity for freshwater rivers and lakes as well as slightly brackish water. The graph at Figure 14.5 shows that there is not a linear relationship between TDS and conductivity over the whole range plotted.



**Figure 14.5**

Conductivity can be related to the total dissolved solids. There is not a linear relationship over all concentration ranges.

Waterwatch Australia is a national community water quality monitoring network that constantly monitors the health of our river systems. Maximum conductivities called ‘trigger values’ have been established for different river systems. Upland rivers and lakes in the tropical north and in south-east Australia typically have trigger values of  $20 \mu\text{S}/\text{cm}$ , whereas lowland rivers in south-central Australia have higher trigger values ( $5000 \mu\text{S}/\text{cm}$ ). Whenever conductivities exceed these trigger values, rapid action needs to be taken to reduce salinity.

### SAMPLE PROBLEM 14.4

#### SOLUTION

A sample of river water was tested with a conductivity meter and gave a reading of  $1100 \mu\text{S}/\text{cm}$  at  $25^\circ\text{C}$ . Use Figure 14.5 to determine the TDS for the water.

The TDS is 600 ppm from the graph. This water is only marginally suitable in terms of potability.

**hard water:** water that will not produce a lather with soap

**soft water:** water that readily lathers with soap

### Testing for hardness

Water can be classified as **hard** or **soft water**. Mineral waters that contain appreciable levels of calcium and/or magnesium ions are described as hard. Hard water is usually associated with the presence of hydrogen carbonate ions, chloride ions and sulfate ions due to the geology of the areas through which the waterways run. Limestone rocks are usually associated with hard water. Porous limestone soils are naturally acidic due to the high levels of carbon dioxide present. This acidic water seeps through cracks in these rocks and dissolves the calcium carbonate and produces a solution of calcium hydrogen carbonate. Soap will not lather in such a solution.



Table 14.4 provides data on the range of concentrations of mineral ions in hard and soft water. The data is reported in terms of the equivalent mass (in milligrams) of calcium carbonate per litre of water.

**Table 14.4** Hard and soft water

Total water hardness classification	soft	moderately hard	hard	very hard	saline
Total hardness (ppm)*	< 60	61–120	121–180	181–500	>500

(\* ppm = mg CaCO<sub>3</sub>/L; includes both calcium and magnesium ion hardness expressed as equivalent CaCO<sub>3</sub>.)

Hard water may be further classified as ‘temporarily hard’ or ‘permanently hard’. Temporarily hard water can be softened by boiling. This process reverses the above equilibrium and removes calcium ions from the water.



Permanently hard water, however, cannot be softened by boiling. This may be due to the presence of magnesium ions rather than calcium ions or the absence of hydrogen carbonate ions.

Water hardness can be tested for using qualitative and quantitative tests. In the field, a calcium ISE is commonly used.

### Qualitative test for hardness

Samples of water can be shaken in stoppered test tubes with flakes of soap or a soap solution. After strong agitation for a minute, the tubes are allowed to stand. Soft water produces significant lather whereas hard water produces only a scum that floats on the water surface. This scum is composed of a precipitate formed between long-chain soap ions and calcium or magnesium ions. The following equation shows a stearate ion from a typical soap forming insoluble calcium stearate.



**Figure 14.6**

Soap solution can be used to test for water hardness.

### Quantitative tests for hardness

Two examples of important quantitative tests for hardness are EDTA titration and atomic absorption spectrophotometry.

#### EDTA titration

The hardness of a water sample can be determined by a titration using a standard solution of a reagent called EDTA. This chemical reacts with metal ions ( $M^{2+}$ ) such as magnesium and/or calcium ions to form a metal-EDTA complex. The reaction stoichiometry is 1 : 1.

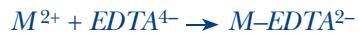
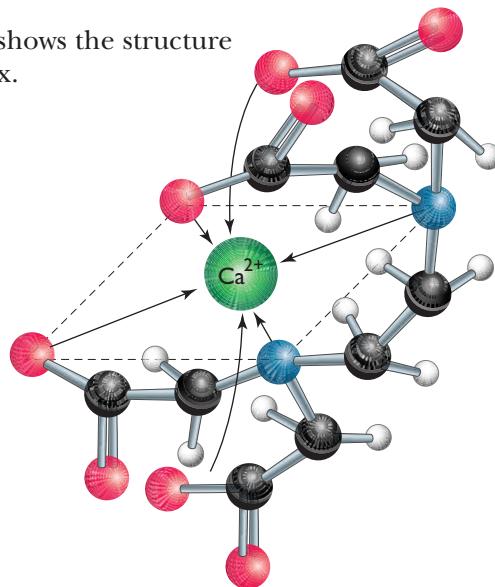


Figure 14.7 shows the structure of this complex.



**Figure 14.7**

EDTA is a complexing agent that binds with metal ions in a 1:1 complex.

### SAMPLE PROBLEM 14.5

### SOLUTION

A pipette was used to deliver a 25.00 mL aliquot of hard water to a conical flask. The water was buffered to a pH of 10 using an ammonia-ammonium chloride buffer. Three drops of Eriochrome Black-T indicator were added and a standard solution of 0.010 mol/L EDTA was added from a burette. The end point was reached when the solution turned from red to blue. The average titre was 7.4 mL. Calculate the total hardness of the water. Express your answer in the units of mg(CaCO<sub>3</sub>)/L.

The water may contain magnesium ions, but they are treated as equivalent calcium ions in this titration.

Step 1. Calculate the number,  $n$ , of moles of EDTA at the end-point.

$$\begin{aligned}n(\text{EDTA}) &= cV = (0.010)(0.0074) \\&= 7.4 \times 10^{-5} \text{ mol}\end{aligned}$$

Step 2. Calculate the number of moles,  $n$ , of equivalent calcium carbonate.

The reaction stoichiometry is 1:1

$$\begin{aligned}n(\text{Ca}^{2+}) &= n(\text{EDTA}) \\&= 7.4 \times 10^{-5} \text{ mol}\end{aligned}$$

$$\begin{aligned}n(\text{CaCO}_3) &= n(\text{Ca}^{2+}) \\&= 7.4 \times 10^{-5} \text{ mol}\end{aligned}$$

Step 3. Calculate the hardness.

$$\begin{aligned}M(\text{CaCO}_3) &= 100.09 \text{ g/mol} \\m(\text{CaCO}_3) &= n.M (\text{CaCO}_3) = (7.4 \times 10^{-5})(100.09) \\&= 7.41 \times 10^{-3} \text{ g} \\&= 7.41 \text{ mg}\end{aligned}$$

$$\begin{aligned}\text{Total hardness} &= 7.41 \text{ mg per } 0.025 \text{ L} \\&= 296 \text{ mg(CaCO}_3\text{)/L}\end{aligned}$$

According to Table 14.4, this water sample is classified as ‘very hard’.

### Atomic absorption spectrophotometry

Atomic absorption spectrophotometry (AAS) can be used to determine the calcium ion and magnesium ion concentrations of water samples. The calcium ion concentration is determined first with a calcium lamp and calcium standards for the calibration graph. The process is repeated with a magnesium lamp and magnesium standards. The total hardness can be calculated by combining this separate data.

#### SAMPLE PROBLEM 14.6

#### SOLUTION

A sample of river water was tested for calcium and magnesium ions using AAS. The results were:

$$c(\text{Ca}^{2+}) = 20 \text{ mg/L}$$

$$c(\text{Mg}^{2+}) = 15 \text{ mg/L}$$

Use this data to determine the total hardness of the water (in units of ppm or  $\text{mg}(\text{CaCO}_3)/\text{L}$ ).

Use 1 litre of water for the calculation.

Step 1. Calculate the equivalent mass,  $m$ , of calcium carbonate.

$$\begin{aligned}m(\text{Ca}^{2+}) &= 20 \text{ mg} \\&= 0.020 \text{ g}\end{aligned}$$

$$\begin{aligned}n(\text{Ca}^{2+}) &= m/M = 0.020/40.08 \\&= 4.99 \times 10^{-4} \text{ mol} \\&= n(\text{CaCO}_3)\end{aligned}$$

$$\begin{aligned}m(\text{CaCO}_3) &= nM(\text{CaCO}_3) = (4.99 \times 10^{-4}) (100.09) \\&= 0.0499 \text{ g} \\&= 50 \text{ mg}\end{aligned}$$

Step 2. Calculate the number of moles of magnesium ions.

$$\begin{aligned}m(\text{Mg}^{2+}) &= 15 \text{ mg} \\&= 0.015 \text{ g} \\n(\text{Mg}^{2+}) &= m/M = 0.015/24.31 \\&= 6.17 \times 10^{-4} \text{ mol}\end{aligned}$$

Step 3. Calculate the equivalent mass of calcium carbonate. Each magnesium ion is equivalent in hardness to one calcium ion.

$$\begin{aligned}m(\text{CaCO}_3) &= nM(\text{CaCO}_3) = (6.17 \times 10^{-4}) (100.09) \\&= 0.0618 \text{ g} \\&= 62 \text{ mg}\end{aligned}$$

Step 4. Calculate the total hardness.

$$\begin{aligned}\text{Total hardness} &= 50 + 62 \\&= 112 \text{ mg}(\text{CaCO}_3)/\text{L}\end{aligned}$$

Step 5. Classify the water sample based on the total hardness.

This water is classified as ‘moderately hard’.

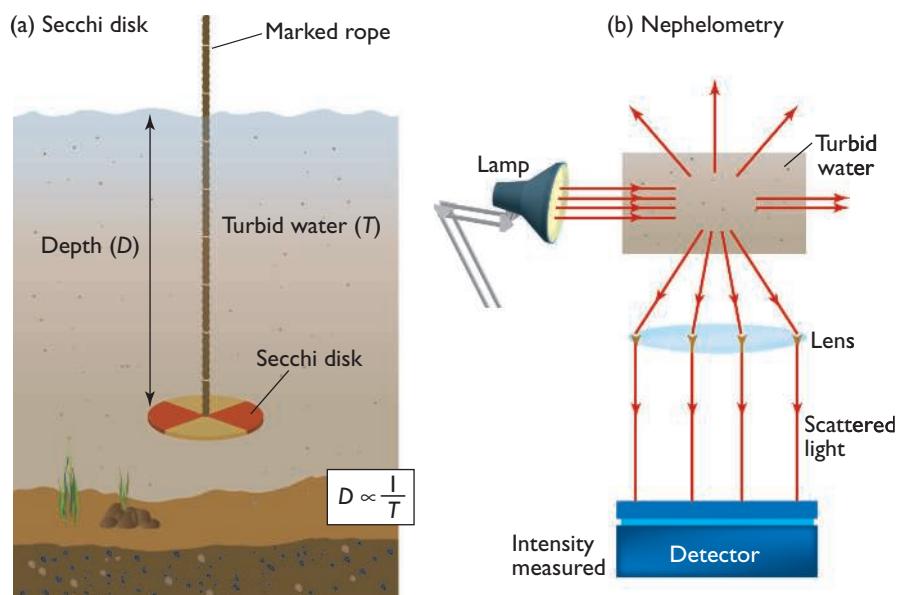
### Testing for turbidity

After rain, soil is often washed into rivers or lakes. The insoluble material becomes suspended in the water and the water looks cloudy or turbid. Clay particles can form colloids in water that scatter light and make the water appear cloudy.

**turbidity:** a measure of cloudiness or lack of transparency of a body of water

**Turbidity** is measured in nephelometric turbidity units (NTU). Potable water should have a turbidity between 1 and 3 NTU. Water at Warragamba Dam typically has a turbidity of 0.1 NTU. Aquatic life will not survive in water that has a turbidity greater than 25 NTU. Aquatic plants cannot photosynthesise if too little light penetrates the water, as this has a significant impact on other organisms along the food chain.

Turbidity can be measured in a number of ways. One method is to measure the total suspended solids (TSS). This is done by filtering a one-litre sample of the water and measuring the dry mass (in milligrams) of the suspended solids collected in the filter. Freshwater streams should not have a TSS greater than 20 mg/L. A second method involves the use of a Secchi disk. The disk is painted with black and white panels. It is lowered into the water with a marked rope until a point is reached where the disk just disappears when viewed through an underwater viewer at the surface. The depth at which this occurs is an inverse measure of the turbidity of the water.



**Figure 14.8**

The Secchi disk is lowered into the water until the disk just disappears.

Nephelometry is an instrumental technique that measures the extent of light scattering.

**nephelometer:** an instrument used to measure turbidity by the extent to which light is scattered by suspended particles in a liquid

A more exact measure of turbidity involves the use of a turbidity meter or **nephelometer**. This instrumental technique measures the intensity of light scattered at  $90^\circ$  to its original path. If the water sample is clear, no light is scattered at right angles to the path. The more turbid the water the more scattering occurs. Nephelometers are supplied with a standard colloidal polymer suspension called *formazin*. This standard typically has a turbidity of 100 NTU. It is used along with distilled water to calibrate the turbidity meter. A linear turbidity response scale (0–100 NTU) is established and the turbidity of unknown water samples can then be measured. If the water sample is highly turbid, it must be systematically diluted with distilled water before measurements are taken.

### SAMPLE PROBLEM 14.7

A turbidity meter is connected to a data logger and the meter is calibrated with a standard formazin suspension (100 NTU) and distilled water (0 NTU). A 5.0 mL sample of highly turbid river water is diluted systematically to a total volume of 25.0 mL. The turbidity of the diluted sample is found to be 12 NTU. Determine the turbidity of the original river water.

## SOLUTION ➤➤➤➤

Step 1. Calculate the dilution factor.

$$\begin{aligned}\text{Dilution factor} &= 25/5 \\ &= 5 : 1\end{aligned}$$

Step 2. Calculate the turbidity.

$$\begin{aligned}\text{Turbidity of river water} &= 12 \times 5 \\ &= 60 \text{ NTU}\end{aligned}$$

## Testing for acidity

Clean potable water should have a pH in the range from 6.5 to 8.5. If the pH drops below 6.5 or rises above 8.5, the water is polluted. Acid rain can cause some lakes to reach critically low pH levels ( $\text{pH} = 4$ ) at which most aquatic organisms die. Acidic water also causes problems for water distribution systems as it leads to corrosion of metal pipes. At pHs above 9.0, aquatic organisms suffer from toxic ammonia poisoning as ammonium ions in the water are converted to ammonia. Acidic or alkaline waste discharges from industries can cause local changes in water pH.

Using pH meters is the simplest way to measure the pH of a sample of water. The pH glass electrode must be properly maintained and calibrated using buffers, otherwise the pH readings are invalid. The pH electrode is a further example of an ion-selective electrode. Narrow-range universal pH papers can also be used to give an accurate measurement of acidity.

## Testing for dissolved oxygen

A high level of **dissolved oxygen (DO)** is vital for water quality. Aquatic animals rely on dissolved oxygen for their respiratory needs. Below 5 ppm of dissolved oxygen, most aquatic organisms exhibit respiratory distress. Table 14.5 provides information about water quality and dissolved oxygen.

Table 14.5 Dissolved oxygen and water quality at 25°C

DO (ppm) at 25°C	6–8	4–6	2–4	<1
Water quality	healthy	moderately polluted	severely polluted	dead

Water becomes oxygenated in a variety of ways. Some oxygen dissolves directly out of the air. Increasing the surface area of the water in contact with the air accelerates this process. Water turbulence and droplet formation (water spray in a waterfall) assist in this process.



Aquatic plants and phytoplankton also generate oxygen by photosynthesis. Some of this oxygen dissolves in the water.

The concentration of dissolved oxygen in water depends on a number of factors including temperature, solute concentration, pollutants and contact with atmospheric oxygen. Salt water, for example, contains less dissolved oxygen than fresh water at the same temperature. Industrial organic waste requires oxygen for its degradation and this puts a demand on oxygen levels. Figure 14.9 shows a graph of dissolved oxygen levels as a function of temperature in fresh water. The higher the temperature the lower the concentration of dissolved oxygen.

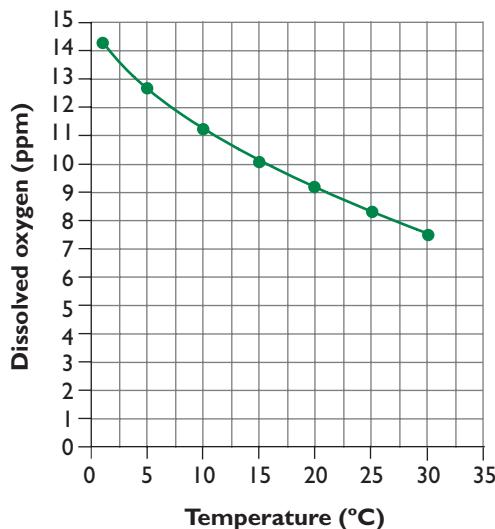


Figure 14.9

The dissolved oxygen levels in water decrease with temperature.

## SYLLABUS FOCUS

### 28. USING INSTRUCTION TERMS CORRECTLY

When answering questions, it is important to know what the instruction terms ('verbs') require you to do. Here is an example:

#### 'Extrapolate'

This instruction word requires you to make an inference from what is known.

#### *Example:*

The following data shows the concentration of oxygen in water as a function of temperature. Extrapolate the data to predict the concentration at a temperature of 35°C.

Temperature (°C)	10	15	20	25	30	35
Dissolved oxygen (ppm)	11.3	10.1	9.1	8.2	7.5	?

#### *Answer:*

For each fall in temperature of 5°C, the differences in dissolved oxygen are not constant, but are decreasing steadily (1.2, 1.0, 0.9, 0.7). Extrapolation of the data leads to a prediction that the DO at 35°C will be 7.0 ppm.

Dissolved oxygen levels can be measured in several ways. Important examples include instrumental methods like the potentiometric oxygen probe and the polarographic oxygen probe, and volumetric methods like the Winkler titration.

### Instrumental method 1 – Potentiometric oxygen probe

A number of oxygen probes are commercially available to measure the dissolved oxygen in water. One probe uses a thallium oxygen-sensitive electrode connected to a reference electrode as part of a galvanic cell. A change in electrode potential is produced as oxygen in the water reacts with thallium (II) ions. The probe is calibrated with solutions of known oxygen concentrations and a linear calibration graph is internally established. These instruments give a direct readout of DO.

### SAMPLE PROBLEM 14.8

Six solutions with known dissolved oxygen concentrations were used to calibrate the oxygen electrode. The results collected were:

Concentration of dissolved oxygen [O <sub>2</sub> ] (ppm)	1.00	3.0	5.0	7.0	10.00	14.0
log [O <sub>2</sub> ]	0.0	0.48	0.70	0.85	1.00	1.15
Voltage (mV)	0	28	41	50	59	68

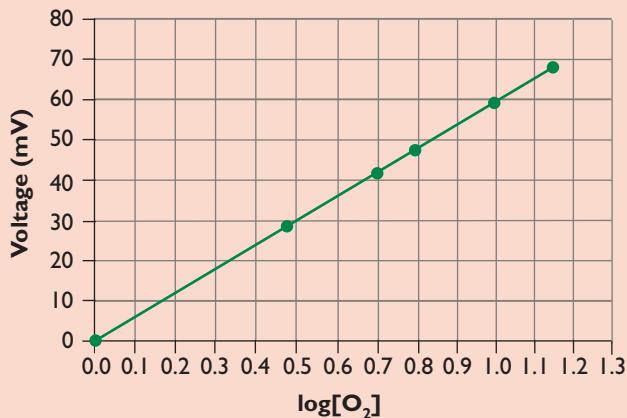
The oxygen electrode and data logger were used to establish a linear relationship between log [O<sub>2</sub>] and voltage, and this relationship was used to determine the dissolved oxygen concentration of an unknown water sample. A sample of polluted water was tested and the voltage recorded was 30 mV.

Use the data to determine the dissolved oxygen concentration in the polluted water sample.

## SOLUTION

The calibration graph is shown in Figure 14.10. Reading from the graph, the value of  $\log [O_2]$  was found to be 0.50.  
Thus the dissolved oxygen concentration in the water sample was:

$$\begin{aligned}D.O &= 10^{0.50} \\&= 3.2 \text{ ppm}\end{aligned}$$



**Figure 14.10** The voltage versus  $\log[O_2]$  graph is used as a calibration graph.

### Instrumental method 2 – Polarographic oxygen probe

The polarographic oxygen probe consists of a platinum disk cathode and a silver ring anode separated by a potassium chloride electrolyte. A porous membrane is permeable to dissolved oxygen that diffuses across the membrane from the water sample into the electrolyte. A constant polarising voltage (e.g. 800 mV) is established across the electrodes and as oxygen diffuses into the cell a tiny current flows. The size of the current depends on the rate of oxygen diffusion and the external dissolved oxygen levels. Continuous stirring is essential to ensure accurate measurements of DO.

### Volumetric method – The Winkler titration

The Winkler titration involves the volumetric determination of dissolved oxygen. It is used to establish the oxygen reference standards for the oxygen sensors discussed previously.

The Winkler method employs a series of steps. The first step involves the quantitative reaction between dissolved oxygen and manganese (II) ions in alkaline solution. In the second step, acidified potassium iodide solution is added and molecular iodine is generated. The amount of iodine generated is determined in the final step by titration with a standard sodium thiosulfate solution using a starch indicator. The overall reaction is:



The analysis requires that water samples which are collected are free of sediment and are sealed underwater so that no air bubbles are present. The temperature of the body of water should also be noted during collection. Winkler field kits have been developed to conduct measurements on site.

## SAMPLE PROBLEM 14.9

### SOLUTION

A 100 mL sample of water ( $20^{\circ}\text{C}$ ) was collected from a lake on a field trip. The sealed sample was later analysed using the Winkler method. Prior to the titration, several millilitres of fresh starch solution were added to the 100 mL treated water sample in a conical flask. The mixture was titrated with a 0.010 mol/L sodium thiosulfate solution. The end point was reached at 9.60 mL.

Calculate the dissolved oxygen concentration in the water.

**Step 1.** Calculate the number of moles of thiosulfate ions added to the flask.

$$\begin{aligned}n(\text{S}_2\text{O}_3^{2-}) &= cV = (0.010)(9.60 \times 10^{-3}) \\&= 9.60 \times 10^{-5} \text{ mol}\end{aligned}$$

**Step 2.** Calculate the number of moles of dissolved oxygen in the 100 mL sample.

The balanced equation (page 330) shows the following stoichiometry.



$$\begin{aligned}\text{Thus, } n(\text{O}_2) &= 1/4 \times n(\text{S}_2\text{O}_3^{2-}) \\&= 2.4 \times 10^{-5} \text{ mol}\end{aligned}$$

**Step 3.** Calculate the mass of dissolved oxygen.

$$\begin{aligned}m(\text{O}_2) &= n(\text{O}_2)M(\text{O}_2) = (2.4 \times 10^{-5})(32.0) \\&= 7.7 \times 10^{-4} \text{ g} \\&= 0.77 \text{ mg}\end{aligned}$$

**Step 4.** Calculate the dissolved oxygen concentration.

$$\begin{aligned}\text{DO} &= 0.77 \text{ mg O}_2 / 0.100 \text{ L water} \\&= 7.7 \text{ mg/L} \\&= 7.7 \text{ ppm}\end{aligned}$$

(Note: At  $20^{\circ}\text{C}$ , the DO for saturated water is 9.1 ppm.)

## Testing for biochemical oxygen demand (BOD)

Whenever organic matter is present in water, microscopic decomposers use it as a food source. These microbes aerobically respire the organic matter and use dissolved oxygen in this respiration process.

Bodies of water that contain large amounts of organic matter (for example, sewage effluent and effluent from abattoirs) can become seriously depleted in oxygen as aerobic microbes respire the waste or oxidise the iron salts. The drop in oxygen levels in the water will seriously affect the aquatic organisms that live in this waterway. Ponds and slow moving streams can become stagnant and toxic if fresh water does not flush out the organic waste.

Environmental chemists can measure the extent of oxygen demand on a waterway using the 5-day **biochemical oxygen demand (BOD)** test. The five-day period has been selected as a standard, even though waste may not be completely respired in such a time. Five days is usually sufficient time for natural organic waste to be decomposed in non-polluted waterways.

**biochemical oxygen demand (BOD):** the quantity of oxygen that is required by decomposers to respire organic waste (and to oxidise certain inorganic materials such as iron) in a body of water.  $\text{BOD}_5$  is the five-day BOD. This measures the change in DO over a 5-day period when the water sample is held in the dark at  $20^{\circ}\text{C}$ .

## BOD of unpolluted water

The 5-day biochemical oxygen demand ( $\text{BOD}_5$ ) can be determined in unpolluted water by conducting two measurements of dissolved oxygen (DO) five days apart. The DO of a water sample is measured at the time of collection using an oxygen probe. A second sample is stored in the dark at  $20^\circ\text{C}$  in a filled, closed incubation bottle for five days, then its DO is measured. The sample is held in the dark to prevent any photosynthetic algae from generating oxygen. The  $\text{BOD}_5$  is then calculated using the equation:

$$\text{BOD}_5 = (\text{DO})_{0 \text{ days}} - (\text{DO})_{5 \text{ days}}$$

### SAMPLE PROBLEM 14.10

A water sample was collected from a stream several kilometres from a waterfall in the mountains. A BOD analysis was performed by measuring the DO at the start and end of a 5-day period. The results were:

$$\begin{aligned}\text{Initial DO} &= 8 \text{ ppm} \\ \text{5-day DO} &= 6 \text{ ppm}\end{aligned}$$

Calculate the 5-day BOD.

$$\text{BOD}_5 = \text{DO}_0 - \text{DO}_5 = 8 - 6 = 2 \text{ ppm}$$

This low  $\text{BOD}_5$  is typical of a sample from clean stream water. There is sufficient oxygen in the water for the oxygen demands of the decomposers to remove natural organic waste.

### SOLUTION

## BOD of polluted water

In this section, we examine how the BOD of polluted water can be determined by (a) diluting with a standard nutrient solution, (b) re-aerating with oxygen and (c) using a respirator.

### Diluting with a standard nutrient solution

The BOD of a waterway that is severely polluted with organic waste cannot be determined as simply as shown in the previous example. The normal DO of water at  $20^\circ\text{C}$  is 9 ppm. This amount of oxygen is readily consumed by microbial respiration over a 5-day period when the water sample has a BOD much higher than 9 ppm. In these cases two methods can be used to measure the BOD.

One method involves systematically diluting the water sample with a special standard aerated nutrient solution (2% glucose–glutamic acid) inoculated with aerobic bacteria. This inoculated nutrient solution has a known  $\text{BOD}_5$ . The diluted water sample's  $\text{BOD}_5$  is then measured and the  $\text{BOD}_5$  of the original undiluted water sample calculated.

### SAMPLE PROBLEM 14.11

A polluted water sample was collected from a river downstream from an untreated domestic sewage outfall. The sample was diluted 1 in 100 with a standard (aerated) inoculation solution that has a known  $\text{BOD}_5$  of 3 ppm. The DO of the diluted sample was then measured after 5 days. The results were:

$$\begin{aligned}\text{Initial DO of diluted sample} &= 8 \text{ ppm} \\ \text{Five-day DO of diluted sample} &= 2 \text{ ppm}\end{aligned}$$

Calculate the 5-day BOD for the river water.

**SOLUTION**

Step 1. Calculate the  $\text{BOD}_5$ .

$$\text{BOD}_5 \text{ of diluted sample} = 8 - 2 = 6 \text{ ppm}$$

Step 2. Subtract the BOD of the nutrient inoculant.

Approximately 3 ppm of this BOD is due to the nutrient inoculant solution. The remainder ( $6 - 3 = 3$  ppm) is due to the diluted water sample.

Step 3. Calculate the true BOD of the undiluted sample.

This sample has been diluted by 1 : 100.

$$\begin{aligned}\text{Thus, the } \text{BOD}_5 \text{ for the river water} &= 3 \times 100 \\ &= 300 \text{ ppm}\end{aligned}$$

**Re-aerating with oxygen**

A second method for determining BOD in polluted water employs the re-aeration of the sample with oxygen every few days until the organic waste is respired. A simple aquarium air pump can be used to bubble air through the sample to provide aeration. The following example illustrates this technique.

**SAMPLE PROBLEM 14.12**

A slightly polluted water sample was collected from a river. The initial DO of the sample was recorded. The sample bottle was stored in the dark at 20°C. After 3 days the DO was again recorded, the sample aerated for 10 minutes and the DO remeasured. The sample was then left for a further 3 days and the DO again measured. The sample was re-aerated for a second time and the DO measured after aeration. After 5 days the DO was remeasured. The results are shown below:

Day 0:	$\text{DO}_0 = 9.0 \text{ ppm}$
Day 3:	$\text{DO}_3 = 3.5 \text{ ppm}$
Day 3 (after aeration):	$\text{DO}_3 = 9.0 \text{ ppm}$
Day 6:	$\text{DO}_6 = 3.8 \text{ ppm}$
Day 6 (after aeration):	$\text{DO}_6 = 9.0 \text{ ppm}$
Day 11:	$\text{DO}_{11} = 5.8 \text{ ppm}$

Calculate the BOD of the water sample.

Step 1. Calculate the change in DO in the first 3 days.

$$\begin{aligned}\Delta\text{DO}_{\text{First 3 days}} &= \text{DO}_0 - \text{DO}_3 = 9.0 - 3.5 \\ &= 5.5 \text{ ppm}\end{aligned}$$

Step 2. Calculate the change in DO in the next 3 days.

$$\begin{aligned}\Delta\text{DO}_{\text{Second 3 days}} &= \text{DO}_3 - \text{DO}_6 = 9.0 - 3.8 \\ &= 5.2 \text{ ppm}\end{aligned}$$

Step 3. Calculate the change in DO in the last 5 days.

$$\begin{aligned}\Delta\text{DO}_{\text{Last 5 days}} &= \text{DO}_6 - \text{DO}_{11} = 9.0 - 5.8 \\ &= 3.2 \text{ ppm}\end{aligned}$$

Step 4. Calculate the total BOD.

$$\begin{aligned}\text{BOD} &= 5.5 + 5.2 + 3.2 \\ &= 13.9 \text{ ppm}\end{aligned}$$

**SOLUTION**

### Using a respirator

The newest method of measuring BOD involves the determination of depleted oxygen in the closed air above a sample of water using a respirometer. The water sample is placed in a special sample bottle with a pressure sensor in the lid. As aerobic respiration occurs in the water, the oxygen becomes depleted and is replaced by diffusion into the water from the air in the bottle. Any carbon dioxide released into the air space is absorbed by an alkaline absorbent. The net reduction in pressure in the air space above the water is a direct measure of the BOD of the water sample.

These commercial units have digital readouts which convert pressure data to BOD values in parts per million. Severely polluted samples (up to 400 000 ppm BOD) can be measured using this technique.

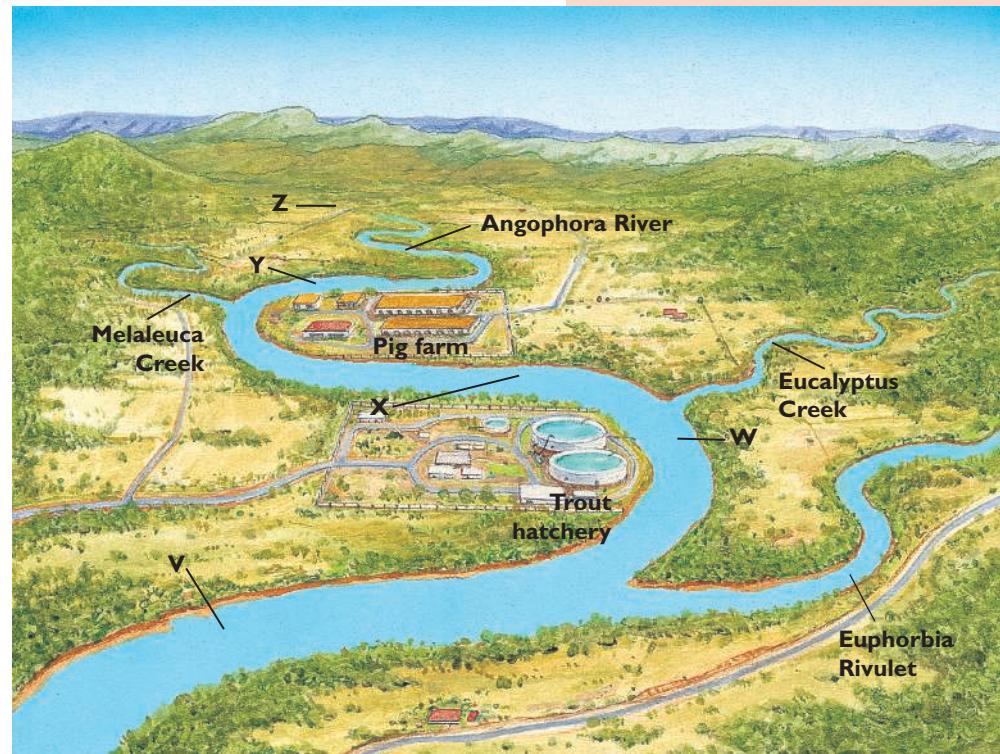
Table 14.6 lists some typical BOD values for polluted waterways.

**Table 14.6** BOD values for various bodies of water

Water system	BOD (ppm)
unpolluted water	1–3
polluted water	>5
domestic sewage (untreated)	350
abattoir effluent	2 600
effluent from paper pulp factory	25 000

### SAMPLE PROBLEM 14.13

The Angophora River flows slowly through farming land, as shown in Figure 14.11. Smaller streams are tributaries of the river. A pig farm is located on the banks of the river as shown in the map. Further downstream is a trout hatchery. Water for the trout hatchery is obtained from the river. An environmental team investigated the quality of water at various sites (V to Z) along the river in response to reports from the trout hatchery that the water quality was deteriorating. Water samples were collected and analysed. Some of these results are shown in the table below. The temperature of the river water was measured at 20°C on the day of the sampling.



**Figure 14.11**  
Map of local river system

Site	DO (ppm)	BOD (ppm)	pH
V	4	35	7.7
W	2	55	7.7
X	1	9000	4.1
Y	5	42	7.0
Z	9	1	7.8

- (a) Account for the trends in DO and BOD along the river.
- (b) Explain the sudden drop in pH at site X.

**SOLUTION** >>>

- (a) The water at Z is healthy, but as it flows past the pig farms it becomes contaminated with the farms' wastewater. This wastewater contains substantial amounts of organic matter (e.g. pig manure), which places a high demand on the oxygen dissolved in the water. Consequently, at X the DO is low and the BOD is high. Although the water has partially recovered by the time it gets to the trout hatchery it is still polluted.
- (b) The pig manure is acidic; this causes the pH to drop from 7.8 to 4.1.

## Factors that affect ion concentration in natural waters

The natural concentration of ions in our rivers, streams and lakes can be easily disturbed by natural as well as human activity. Tree removal, intensive farming and irrigation of crops all contribute to change the chemical balance of our soils. This change is reflected in the sub-surface water that contains many dissolved ions.

Salinity of the land is a major problem in many parts of outback Australia. This phenomenon is directly linked to poor land and water management. Surface water run-off after rain from agricultural or industrial land usually leads to increases in the ion contamination of our natural waters. Table 14.7 summarises the factors that can alter the ion concentration in natural waters.

**heavy metals:** metals of high atomic weight that are toxic to humans in relatively low concentrations

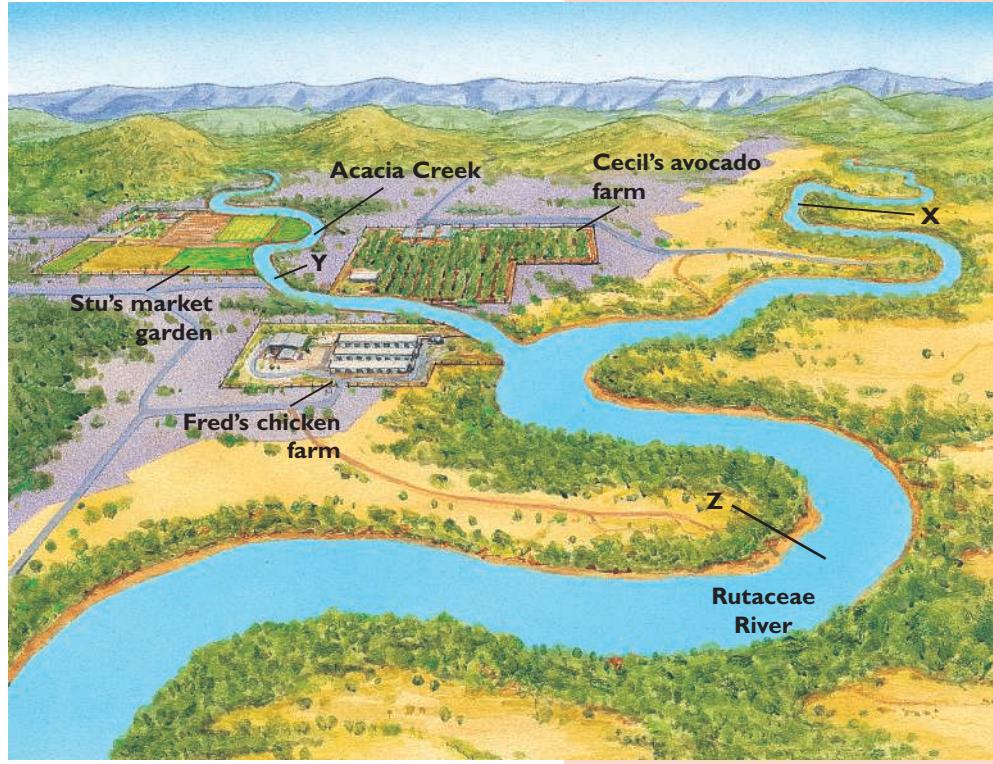
**Table 14.7** Factors that affect the ion concentration in natural waters

Factor	Effect on ion concentration
heavy rain/flooding	Sustained heavy rain will cause large amounts of fresh water to enter a river or lake. The concentration of ions in the water will temporarily decrease due to this additional water. The frequency of heavy rain and flooding will also influence the ion levels in waterways.
pH of rain water	The more acidic the rainwater or ground water, the more minerals that will be dissolved. These dissolved minerals will find their way into rivers and lakes and lead to an increase in the concentration of certain ions (e.g. aluminium ions).
leaching of rocks and soils	Ground water may remain in contact with minerals in the ground for long periods of time. Minerals dissolve in the ground water, which may find its way into lakes and rivers or remain in subterranean aquifers.
differential solubility of rock minerals and soil minerals	Some minerals are more soluble in water than others. Many sulfate and chloride minerals are more soluble than silicate or oxides. Limestone rocks are readily leached and there is a resulting increase in calcium ions and hydrogen carbonate ions.
water temperature	Minerals dissolve faster at higher water temperatures.
rate of evaporation	The concentration of ions in waterways will be affected by the rate of evaporation of the water. In hot climates this rate will increase and the concentration of ions will increase.
agriculture	Farmers usually fertilise their soils to grow crops. Rainwater can carry some of this fertiliser from the soil into rivers and lakes. There are often increases in nitrate ion, ammonium ion and phosphate ion concentrations as a result of this process. Leaching of animal faeces on grazing properties will contribute to increased concentrations of nitrogen and phosphorus in waterways.
aquatic organisms	The activity of aquatic invertebrates and water plants can change the balance of ions in a body of water. Many shelled invertebrates utilise calcium ions and carbonate ions to construct their exoskeletons or shells.
industrial effluent	Various industries are allowed to discharge diluted waste into rivers. Some of this waste leads to increases in ion levels including pollution by <b>heavy metal</b> ions

In comparison with freshwater rivers and lakes, the oceans of the world have fairly constant concentrations of ions. Look back to Table 14.1 to review the high levels of these ions in sea water.

### SAMPLE PROBLEM 14.14

A team of environmental chemists investigated the water quality in Acacia Creek and Rutaceae River after a month without rain in the area. Figure 14.12 shows a map of this area including the rocks of the surrounding countryside and the location of various human activities such as farms.



**Figure 14.12**  
Map of Acacia Creek and Rutaceae River

Water was sampled at two locations in the river (Sites X and Z) and one in the creek (Site Y) on three days in winter (July 10, 12, and 14). On July 11, heavy rains fell over the area of study for 12 hours. Table 14.8 shows some of the results of the investigation.

Use this data to answer the following questions.

- The table shows that there has been a turbidity increase in Acacia Creek between July 10 and July 12. Explain the cause of this increase.
- Weathering and erosion of the rocks and soil will increase the amount of suspended and dissolved solids in the creek and river. Use the tabulated data and map to identify whether sandstone or shale is more readily weathered and eroded.
- The table shows that the ammonium ion concentration in the water at Sites Y and Z increased from July 10 to July 12. Account for this increase.
- The environmental team estimated that about 20% of the water at Site Z in the Rutaceae River came from Acacia Creek. Use the data to justify this estimation.

**Table 14.8** Selected results of water quality investigation

Date	July 10			July 12			July 14		
	X	Y	Z	X	Y	Z	X	Y	Z
Water temperature (°C)	14	16	15	13	14	14	14	15	15
Turbidity (NTU)	5	11	7	6	44	14	5	27	10
[NH <sub>4</sub> <sup>+</sup> ] (ppm)	5	7	6	4	17	9	5	9	7
[Ca <sup>2+</sup> ] (ppm)	3	24	7	3	27	9	3	25	8
[Cl <sup>-</sup> ] (ppm)	34	320	92	29	375	117	32	310	97

**SOLUTION** >>>
**14.1 PRACTICAL ACTIVITIES**  
  
 Testing water samples

**14.2 DATA ANALYSIS**  
  
 Testing for heavy metal pollution and eutrophication

- (a) The information states that there was heavy rain on July 11. This rain will have washed soil from the land into Acacia Creek and the Rutaceae River. This suspended material will cause a temporary increase in turbidity of the water.
- (b) Shale is more readily weathered and eroded by running water. The table shows that at Site Y (compared with Site X) there is greater turbidity (suspended solids) and higher concentrations of dissolved ions. Site Y data comes from creek water that has flowed through shale rocks whereas Site X data comes from water that has flowed through sandstone rocks.
- (c) Ammonium ions are present in fertilisers. The rain on July 11 probably caused water run-off from the farms to enter the river. This run-off would contain soluble material from the fertilisers used in the soil.
- (d) Use the chloride ion data for July 10 (after the rain, the data is not reliable to do this calculation). If the Creek (at Y) contributes 20% of the flow at site Z and 80% comes from the river (at X), then:

$$[\text{Cl}^-] \text{ at } Z = 20/100(320)_Y + 80/100(34)_X = 64 + 27.2 \\ = 91.2 \text{ ppm (cf. 92)}$$

Repeat this step for the calcium data.

Use the calcium ion data for July 10.

$$[\text{Ca}^{2+}] \text{ at } Z = 20/100(24)_Y + 80/100(3)_X = 4.8 + 2.4 \\ = 7.2 \text{ ppm (cf. 7)}$$

Thus, the estimation seems reasonably valid.

## 14.1 QUESTIONS

1. Use a specific example to distinguish between a quantitative and a qualitative investigation involving water quality.
2. The following graph shows the solubility of oxygen in water as a function of temperature.

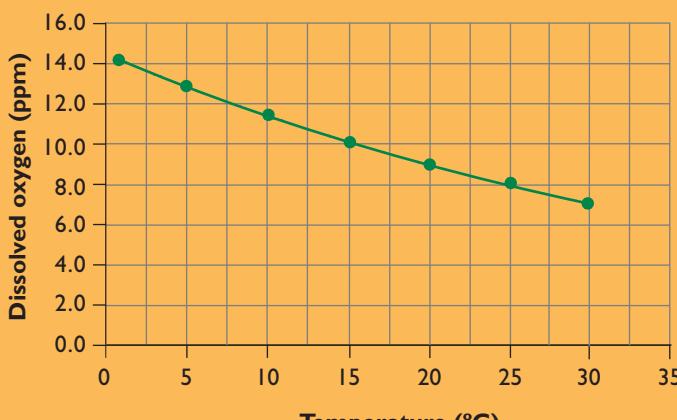


Figure 14.13

The dissolved oxygen content of water in a lake was measured using an oxygen probe. The DO was 4.8 ppm when the water temperature was 16°C. Discuss the quality of this water in the lake.

3. Explain how a long period of rain can affect the concentration of ions in a river.
4. Explain the cause of eutrophication in a river and describe the consequences of a river becoming eutrophic. (Revise Data analysis 14.2 before answering this question.)
5. Compare the methods used to measure the total dissolved solids (TDS) in water.
6. A sample of water has a hardness of 80 mg/L of  $\text{CaCO}_3$ .
  - (a) Define the term 'hardness'.
  - (b) Describe a qualitative test for hardness.
  - (c) Explain how the hardness of the above sample could have been measured.

7. A 5.0 mL sample of river water was diluted with 45 mL of distilled water. The diluted sample's turbidity was measured using a turbidity probe. The result was 9.5 NTU. Determine the turbidity of the original river water.
8. A sample of water is tested for the presence of heavy metals.
  - (a) Identify three heavy metals that can pollute waterways.
  - (b) Identify a quantitative technique to measure the levels of these heavy metal pollutants.
  - (c) A sample of polluted water was tested qualitatively using ion tests. Explain how these tests could be used to show that zinc ions were present.
9. The dissolved oxygen content of a 100 mL sample of rapidly flowing river water (at 23°C) was determined using a Winkler titration. The average titre was 4.00 mL of 0.025 mol/L sodium thiosulfate.
  - (a) Calculate the DO for this water sample.
- (b) Determine the percentage saturation of oxygen in the water. (Maximum solubility of oxygen in water = 8.56 ppm at 23°C.)
10. The concentration of carbonate ions in river water was measured using an acid-base titration. A 1-litre sample of river water was concentrated until the volume of water was 100 mL. This 100 mL sample of the concentrated river water was titrated with 0.010 mol/L hydrochloric acid using phenolphthalein indicator. An end point was achieved at 6.00 mL.
  - (a) The neutralisation reaction involves the partial neutralisation of carbonate ions to form hydrogen carbonate ions. Write a balanced ionic equation for this reaction.
  - (b) Describe the colour change of the phenolphthalein indicator at the end point.
  - (c) Calculate the molarity of carbonate ions in the normal river water.
  - (d) Explain why methyl orange would not be a suitable indicator for this titration.

## 14.2 WATER PURIFICATION

### Remember

Before beginning this section, you should be able to:

- outline the significance of water as a natural resource for humans and other organisms
- use cause and effect relationships to explain phenomena.

### Key content

By the end of this section, you should be able to:

- describe and assess the effectiveness of methods used to purify and sanitise mass water supplies
- describe the design and composition of microscopic membrane filters and explain how they purify contaminated water
- gather, process and present information on the features of the local town water supply in terms of (a) catchment area (b) possible sources of contamination in this catchment (c) chemical tests available to determine levels and types of contaminants (d) physical and chemical processes used to purify water and (e) chemical additives in the water and the reasons for the presence of these additives.

Water authorities need to monitor and manage water supplies for towns and cities. Water is used for many purposes including drinking, cooking, washing, irrigating crops and supporting industrial applications. Population centres cannot exist without a regular supply of purified drinking water. The increasing population of Sydney and the changes in climatic patterns have placed drinking water supplies under great pressure. Wastewater also needs to be treated before it is released back into the environment. Chemical and instrumental techniques are used to ensure the quality of our water supplies.

### Production of potable water

The water in storage dams such as Warragamba or Woronora is called 'raw' water. This water is not fit for drinking as it contains suspended and dissolved materials, including biological spores and microbes that could cause disease.



**Figure 14.14a**

Water that is held in a large storage reservoir must be purified before it can be consumed.

**flocculation:** the clumping together of fine colloidal particles following the addition of coagulating chemicals

**sedimentation:** the settling under gravity of suspended particles in water

The stages in the process of converting raw water into potable water are summarised in Table 14.9. These stages involve (a) clarification, to produce clear, colourless water and (b) sanitisation, to ensure that harmful microbes are removed. Not all stages need to be performed if the raw water quality is high.

**Figure 14.14b**

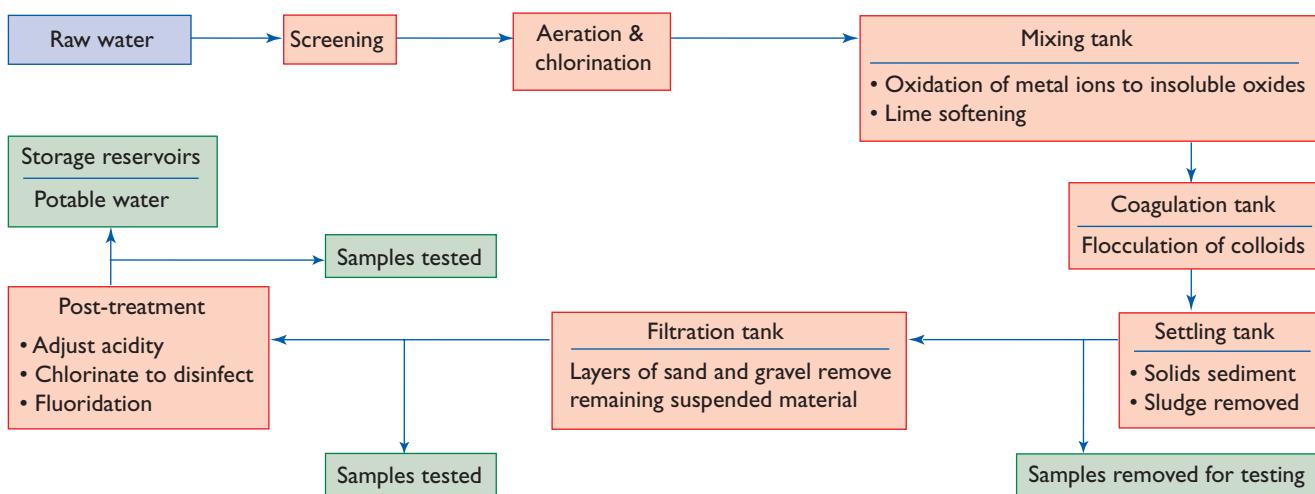
Part of the water purification procedure is filtration to remove suspended solids.



**Table 14.9** Converting raw water into potable water

Stage	Information
screening	Large objects including fish and plant debris are removed using screens (50–100 mesh or 305–140 micrometres) that act as sieves.
aeration and chlorination	In some (but not all) plants, the screened raw water is pumped from the dam to the mixing tank in the filtration plant. It may be: <ul style="list-style-type: none"> <li>(a) aerated by spraying — DO increases and soluble iron and manganese salts are oxidised to remove colour and odour; this aeration process is also used in the latter processes of coagulation and <b>flocculation</b></li> <li>(b) chlorinated to kill disease-causing bacteria.</li> </ul>
mixing tank	Chemicals are added in the mixing tank. <ul style="list-style-type: none"> <li>(a) Potassium permanganate (<math>\text{KMnO}_4</math>). This oxidises any manganese ions to form insoluble manganese dioxide. Iron is also removed by this process as soluble iron is oxidised to form insoluble iron oxides.</li> <li>(b) Lime (<math>\text{CaO}</math>) and soda ash (<math>\text{Na}_2\text{CO}_3</math>). ‘Lime softening’ is used to regulate the levels of calcium and magnesium (to lower hardness levels). The water that emerges is slightly alkaline and pH adjustment is made in post-treatment.</li> </ul>
coagulation tank	Water from the mixing tank passes into the coagulation tank. Chemicals are added to flocculate the fine suspended matter into larger particles so they can be filtered in the next stage. Iron (III) chloride (or, less commonly, aluminium sulfate) and cationic polymers (polyelectrolytes) are added to coagulate colloidal particles to form flocs. The iron (III) ions form gelatinous iron (III) hydroxide that traps the negatively charged colloid particles and form the flocs. $\text{Ca}(\text{OH})_2$ is also added to raise the pH (~7) to allow the flocs to remain stable. The presence of iron (III) ions also precipitates out phosphate ions as iron (III) phosphate.
settling tank	The water is now transferred into the settling tank where the flocs undergo <b>sedimentation</b> . The solid material that collects on the base of the settling tank is called <i>sludge</i> . Particles that are larger than 1000 micrometres (1 mm) tend to sediment to form the sludge. About 90% of particles are removed this way. The sludge is periodically removed and disposed of, or used for composting. The water is then transferred to the filtration tanks.
filtration tanks	Layers of sand and gravel are used to filter the water of any remaining suspended material. The effective pore size of these filters is 100 micrometres. In some plants, granular activated charcoal or anthracite filters are used to remove coloured ions and coloured organic solutes. This also improves water taste. Non-ionic polymers assist in the filtration process by slowing the rate of movement of fine flocs through the filter beds. The turbidity at the end of this stage is usually less than 0.5 NTU and the colour is usually less than 2 HU.
post-treatment	<ul style="list-style-type: none"> <li>(a) Acidity levels: The pH is re-adjusted using hydrated lime/<math>\text{Na}_2\text{CO}_3</math> (or even hydrochloric acid is used for very alkaline water) to prevent scaling and corrosion of pipes in the water distribution pipes.</li> <li>(b) Disinfection: Chlorine and ammonia are added to form monochloramine (<math>\text{NH}_2\text{Cl}</math>), a long-acting disinfectant. Drinking water should contain less than two coliform bacterial units per 100 mL (&lt;2 CFU/100 mL). Coliforms are indicators of faecal contamination. <i>(Note: CFU = colony-forming units)</i></li> <li>(c) Fluoridation: Fluoride ions (~1 ppm) are added (in the form of calcium fluoride, sodium fluoride and sodium silicon fluoride) to provide potable water that will help to reduce tooth decay by hardening tooth enamel.</li> </ul> <p>The treated water is pumped to storage reservoirs (e.g. Prospect) and then through the water distribution pipes to consumers.</p>

Figure 14.15 shows a flow chart that summarises the water purification process.



**Figure 14.15**

Water purification involves many steps before potable water is produced.



### FLOC FORMATION IN WATER PURIFICATION

The effectiveness of these methods can be assessed by comparing some key properties of raw water with those of the potable water produced by the processes discussed above. Table 14.10 shows some typical data for raw water and the purified water produced from it. Water authorities are required by law to comply with Australian Drinking Water Guidelines (ADWG) for water quality in their management of water systems.

**Table 14.10** Comparison of water quality before and after purification

Water property (average)	Raw water	Purified water
pH	7.4	7.7
turbidity (NTU)	5	0.08
iron (ppb)	500	10
manganese (ppb)	30	1
coliform bacteria (cfu/100 ml)	300	<1

### SAMPLE PROBLEM 14.15

A local dam is part of a town's catchment area. Water tests on raw water in the dam were conducted. The water was then treated in a filtration and purification plant. A sample of water was removed at one point in the purification process. The following table provides information on the water quality of the raw sample and the sample of the partly treated water. ADWG values are also tabulated.

Water property	Raw water	Treated water	ADWG
pH	6.2	7.3	6.5–8.5
turbidity (NTU)	3.5	0.1	<5
fluoride (ppm)	0.2	0.2	<1.5
true colour (Hazen units)	70	1.5	<15
iron (ppb)	350	16	<300
manganese (ppb)	250	2	<100

**SOLUTION**

Use this data to:

- Identify the stage in the water purification process when the partly treated sample was taken.
  - Explain the process that has led to each change in property.
  - Assess the effectiveness of the water treatment process in producing potable water for the town.
- (a) Examine the fluoride data in the table. No fluoridation has occurred as the level has stayed the same. The water sample was taken after it had left the filtration tank and after the acidity levels were adjusted. This is one of the latter stages of the purification process.
- (b) pH: Lime and carbon dioxide are used to adjust the pH.  
Turbidity: Reduction achieved by flocculation, sedimentation and filtration  
Colour: Reduced by aeration; passing through a coal bed in the filtration tank  
Iron and Manganese: Reduced by addition of potassium permanganate followed by filtration
- (c) The partial water treatment has been completely effective based on a comparison with the ADWG values and the data from raw and treated water. The turbidity of the water was already within the required levels but the filtration plant has improved the clarity of the water. The pH was too low, and was raised to the guideline range. The raw water had too high a colour and too high a level of metals such as iron and manganese. These have all been reduced to required levels.

## SYLLABUS FOCUS

### 29. USING INSTRUCTION TERMS CORRECTLY

When answering questions, it is important to know what the instruction terms ('verbs') require you to do. Here is an example:

**'Analyse'**

This instruction word requires you to identify components and the relationship between them, or to draw out and relate implications.

***Example:***

The concentration of sulfate ions in natural water can be determined roughly using barium nitrate solutions of varying concentrations. A positive test is the formation of a white suspension of barium sulfate. In each experiment, one drop of the barium nitrate solution is added. The following data shows the relationship between the volume of each barium nitrate solution added, the volume of natural water being tested and the minimum concentration of sulfate at which turbidity is produced due to the precipitation of white barium sulfate.

Analyse the data and draw appropriate conclusions.

***Answer:***

The molarity of the barium ions is decreased by a factor of 10 in each subsequent test. The minimum sulfate that can be detected increases by a factor of 10. Thus, if the sulfate concentration in the natural water is low, then a high molarity barium nitrate solution must be used to detect the sulfate ion. If the level of sulfate is high, then the barium ion solution can be of a lower molarity.

Molarity of the barium nitrate solution (mol/L)	Volume of natural water tested (mL)	Minimum sulfate concentration (ppm)
$10^{-2}$	10	0.5
$10^{-3}$	10	5
$10^{-3}$	100	50
$10^{-4}$	100	500

**eutrophication:** the abundant growth of algae and water plants due to the presence of high levels of nitrogenous and phosphate nutrients in the waterway; (when these plants die their decomposition leads to severe oxygen depletion in the waterway)

## Treatment of wastewater

Household wastewater and small amounts of industrial wastewater as well as domestic sewage water are piped to sewage works for treatment prior to discharge into the environment. Sydney discharges this treated water into the ocean several kilometres off the coast. The treatments used vary from one location to another. Organic solvents cannot be disposed of in sewage lines; they must be collected and disposed of in special sites. Table 14.11 lists the levels of treatment used.

**Table 14.11** Treatment of wastewater

Treatment Level	Information
Primary	<ol style="list-style-type: none"> <li>1. Sewage is screened to remove large objects and other solids.</li> <li>2. Sewage is held in settling tanks. Oils and scum are skimmed off the surface. Sludge collects at the bottom of the tanks.</li> <li>3. Chlorination is used to sanitise the water.</li> <li>4. Water is then released to the environment or treated further.</li> </ol> <p>About 40% of organic pollutants and 60% of suspended solids are usually removed after primary treatment.</p>
Secondary	<p>Wastewater can be further treated rather than being released to the environment at the end of the primary treatment.</p> <ol style="list-style-type: none"> <li>1. The primary effluent passes into a gravel bed in the trickle filter where it is mixed with aerobic bacteria that digest the waste.</li> <li>2. The activated-sludge method also involves bacterial digestion and aeration to promote the removal of oxygen-demanding organic wastes. The BOD of the wastewater is lowered in this process.</li> <li>3. The effluent is then allowed to separate in settling tanks.</li> <li>4. The water is chlorinated or disinfected with UV light before being released into the environment.</li> </ol>
Tertiary	<p>Wastewater can be further purified using tertiary treatment methods. This process is expensive and not commonly used. Some of the methods employed include:</p> <ol style="list-style-type: none"> <li>1. removal of colloidal solids by coagulation</li> <li>2. precipitation of phosphates using lime; this reduces <b>eutrophication</b> when water is released</li> <li>3. adsorption of organic solutes on activated charcoal</li> <li>4. reverse osmosis to remove ions</li> <li>5. ion-exchange resins to remove ions.</li> </ol>

In ion exchange, polymer resins can be used to remove ions from water. In a cation ion-exchange resin, negatively charged functional groups combine with cations in the water and release hydrogen ions from the resin. In anion ion-exchange resins, positively charged functional groups on the resin combine with anions in the water and release hydroxide ions. By combining a cationic and an anionic resin in series, salts can be removed and pure water obtained. Hydrogen ions and hydroxide ions neutralise to form water.

Environmental agencies have developed guidelines for the disposal of industrial wastewater. Toxic materials, including heavy metals, can be released into the environment in wastewater, only if their concentrations do not exceed the published guidelines. Each local water authority uses EPA and ANZECC data to establish local guidelines for effluents and wastewater. These guidelines take into account the dilution effect when the effluent is discharged. The effect of nutrient discharges also needs to be considered. For industrial trade effluents the typical maximum levels of nitrogen and phosphorus are 100 ppm and 20 ppm respectively. For effluents containing lead and cadmium, the typical maximum levels are 10 ppm.

## Microscopic membrane filters

Tertiary treatment of water can be performed using a variety of techniques. Salty and brackish water can be converted to fresh water using techniques such as ion-exchange chromatography and reverse osmosis. Reverse osmosis involves the application of external pressure to an electrolyte solution such that fresh water passes through a semi-permeable membrane and the ions are excluded. This process is used in many localities to produce fresh water from sea water. The concentrated salt water left behind is then discharged back into the ocean.



**Figure 14.16**

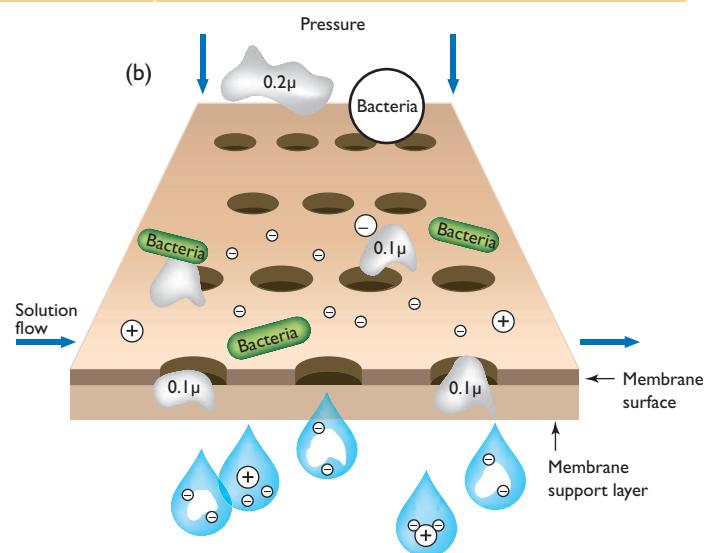
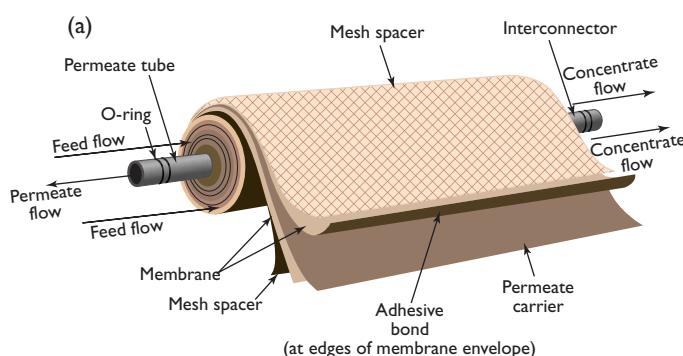
Desalination plants create fresh water from salt water. In some parts of Australia and overseas these plants are the only source of fresh water. They purify water using reverse osmosis.

Membrane filtration is a very effective tertiary treatment of water. Such a system was installed at Olympic Park in Sydney for the games in 2000. This plant purifies recycled water.

The development of new semi-permeable membranes made from polymers has led to new water purification technologies. These technologies are called *microfiltration* (MF), *ultrafiltration* (UF) and *nanofiltration* (NF). Table 14.12 describes some features of each of these filtration techniques. In membrane filtration, water is filtered through tiny holes (or pores) in the polymer membrane wall. The smaller the pore size, the greater the retention of particles present in the water during the filtration process. In all of these technologies, the water to be filtered is run across the surface of the membrane rather than at right angles to it to ensure that the fine pores do not clog up with particles.

**Table 14.12** Microscopic membrane filtration

Technology	Filter pore size (nanometres)	Information
microfiltration	100 – 1000	Microfilters remove fine silt, colloids (200–500 nm in size) and a range of microbes (protozoa, bacteria), but few viruses. This is a common technology used in small rural water-treatment plants. The filters are composed of bundles of hollow polymer threads.
ultrafiltration	5 – 50	Removes all microbes including viruses and some larger organic molecules (molecular weight > 10 000). Water colour is improved. The membranes are typically made of polymers such as polysulfone and cellulose acetate. Ions can be removed only if the membranes have special surfactant coatings (e.g. deoxycholic acid). This method is used in the separation of paint pigments and resins from water.
nanofiltration	0.5–5	Removes all organic molecules with molecular weights down to 300 and some salts containing divalent and trivalent ions. This uses higher operating pressures and costs than ultrafiltration. The membranes are typically composed of polyamide or cellulose acetate polymers. The method is used in kidney dialysis, medicine purification and water softening.
reverse osmosis	0.1–1	Removes all solutes including ions. This process is more expensive than nanofiltration. It is used to desalinate sea water.



**Figure 14.17**

- (a) Spiral bound membrane filter element.
- (b) Membrane filters have various pore sizes. The smaller the pore size the greater the purity of the water produced.

### 14.3 DATA ANALYSIS

Investigating the Sydney water supply

Membrane filters can be manufactured in sheet or capillary form. These membranes are quite strong, as they must withstand high fluid pressures (up to 500 kPa) during the filtration process. The sheet membranes are typically 100 micrometres thick with variable-sized pores. The sheets can be folded by pleating or spirally wound around a core. They are usually housed in an outer plastic container to form a cartridge that can be inserted or removed easily into the water filtration line. The filters can normally be back-flushed and reused. The capillary filters are composed of hollow fibres (inside diameter ~200 micrometres) with pore sizes between 0.2 and 0.5 micrometres. The raw water runs along the outside of the capillary fibres and clean water penetrates the pores to the inside of each capillary.

Larger membrane filter plants have been established in various locations to purify recycled water. Olympic Park in Sydney has a membrane filtration plant that purifies recycled water for use within the park and in the suburb of Newington, which was the site of the athletes' village during the 2000 Olympic Games. Membrane filter plants are also used in industries such as in the production of bottled water, soft drinks and beers. Such plants are not suitable for purifying water directly from a reservoir as the filters would quickly clog up due to the suspended matter.

## 14.2 QUESTIONS

- In some water purification plants, the raw water is sprayed into the air to form a fine mist. The purpose of this process is to
  - acidify the water.
  - coagulate the colloidal particles.
  - increase the dissolved oxygen content.
  - reduce the turbidity.
- Alum rather than iron (III) chloride can be added as part of the water purification process. The purpose of this alum is to
  - flocculate the colloidal particles.
  - acidify the water to remove carbonate deposits.
  - precipitate heavy metals.
  - improve the taste.
- In a water treatment plant, the water passes through layers of sand and gravel. This process is used to
  - increase the BOD of the water.
  - remove phosphates.
  - filter the remaining suspended solids.
  - remove large objects such as plant debris.
- The purpose of chlorination in a water treatment plant is to
  - adjust the pH of the water.
  - soften hard water.
  - assist in flocculating the fine colloidal particles.
  - kill disease-causing microbes.
- Explain the purpose of each process in the primary treatment of sewage effluent.

- The correct sequence in which water is treated in a water treatment plant is
  - screening, mixing, coagulation, settling, filtration and disinfection.
  - screening, coagulation, settling, filtration, mixing and disinfection.
  - disinfection, mixing, settling, filtration, coagulation and screening.
  - screening, filtration, mixing, settling, coagulation and disinfection.
- Australian Drinking Water Guidelines (ADWG) require potable water to have iron concentrations of less than 300 ppb.
  - Explain why levels of iron should be below this level.
  - Explain how iron levels in raw water are reduced during water treatment.
- In some cases secondary treatment follows the primary treatment of wastewater. In this process, aerobic bacteria are added to the treated wastewater.
  - Explain the purpose of these aerobic bacteria.
  - Explain why vigorous aeration is important in the activated sludge process.
  - Describe how the BOD of the water changes during this process.
  - Identify the last step in the secondary treatment before the water is discharged.

9. Membrane filters can be used to further purify drinking water.
- (a) Identify the type of filtration technology that would be sufficient to remove:
- ii(i) parasites such as *Cryptosporidium* and *Giardia*
  - ii(ii) most organic molecules and some highly charged metal ions
- (iii) all solutes including ions.
- (b) Explain how these filters can be cleaned for re-use.
- (c) Explain why the water to be filtered moves across the membrane surface rather than at right angles to it.
10. Compare ultrafiltration membranes to nanofiltration membranes.



[www.jaconline.com.au/chemnsw/chemistry2](http://www.jaconline.com.au/chemnsw/chemistry2)



### MODULE 3 REVISION

## SUMMARY

- Analytical and environmental chemists conduct a range of tests on water to determine its quality.
- Potable water should have low concentrations of ions.
- The level of total dissolved solids should be low in potable water. The TDS value for a water sample can be determined by weighing the residue after evaporation of a known volume of water. It can also be measured using a conductivity meter.
- Hardness in water is caused by the presence of calcium and magnesium ions.
- Potable water should have a turbidity less than 3 NTU.
- Clean potable water should have a pH between 6.5 and 8.5.
- The level of dissolved oxygen in water depends on temperature and the presence of pollutants. Oxygen probes can be used to measure DO levels in water.
- The biochemical oxygen demand is a measure of the degree to which a water sample is polluted by organic matter. Analytical chemists conduct a 5-day BOD test. Unpolluted water should have a BOD of 1–3 ppm.
- The natural concentration of ions in streams and rivers depends on many factors including rain, flooding, leaching of rocks and soil, agriculture, water temperature and rate of evaporation.
- Water must be purified before it is potable. The procedures used to purify water include screening, aeration, coagulating, settling, filtration, adjustment of acidity, disinfection and fluoridation.
- Wastewater can be treated to allow it to be released into the environment. Treatments can be classified as primary, secondary and tertiary.
- Microscopic membrane filters have been developed to remove substances that are not removed in normal treatment processes. Very fine membranes with very small pores can remove viruses, large molecules and some ions.

# PRACTICAL ACTIVITIES

## 14.1

### PRACTICAL ACTIVITIES



## TESTING WATER SAMPLES

### Aim

To use a variety of qualitative and quantitative tests to investigate the quality of water samples

### Safety

- Wear safety glasses throughout this experiment.
- Silver nitrate stains the skin. Potassium chromate solution and barium chloride solution are toxic.
- Identify other safety precautions relevant to this experiment by reading the method.

### Materials

Stoppered samples of some or all of the following are provided in screw-cap bottles. Ensure the bottles are completely filled (there are no air gaps).

- tap water
- boiled tap water allowed to cool
- deionised (distilled) water
- aquarium water
- stagnant water
- water containing organic nutrients (e.g. glucose solution)
- sea water
- stream water
- artificial hard water (calcium chloride solution(0.5 g/L))
- 0.1 molar nitric acid (dropper bottle)
- 0.1 molar silver nitrate (dropper bottle and as a reagent for titration)
- 0.1 molar barium chloride (dropper bottle)
- 0.1 molar potassium thiocyanate (dropper bottle)
- 0.1 molar sodium chloride
- 0.1 molar ammonium molybdate prepared in 5 molar sulfuric acid
- 0.01 mol/L ascorbic acid
- fine soap flakes

- narrow-range universal indicator paper
- quantitative filter paper
- pH meter
- hotplate
- electronic balance
- pipette (25 mL and 10 mL graduated)
- burette
- clock glass
- 10 mL measuring cylinder
- 1 litre beaker
- 500 mL beaker
- 50 mL beaker
- test tubes
- wash bottle
- glass rod

### Method

These tests are best done in teams. Each team can take responsibility for different tests and the results can be combined.

#### (a) Qualitative tests

Qualitative tests are used to identify the presence or absence of an ion or molecule in the water sample. They do not measure the amount or concentration of the substance.

##### Test 1: Hardness

Place 3 mL of each water sample in separate test tubes. Add a spatula tip of fine soap flakes to each tube. Stopper and shake the tube strongly for 1 minute. Place the tubes back in the rack and observe the presence or absence of a lather of soap. You may be able to rank the solutions according to the height of soap foam. Compare with the deionised water sample as a control.

##### Test 2: Dissolved solids

Use filtered samples of each of the supplied water samples.

Place 2 mL of each water sample in a clean 50 mL beaker. Place the beaker on a hot plate and *gently* evaporate the water.

When all the water has evaporated and the beaker has cooled, examine the beaker for any crystals

# PRACTICAL ACTIVITIES

or solid deposits. The greater the amounts of deposit, the more dissolved solids there are in the water sample. Rank (where possible) the water samples in terms of their relative levels of dissolved solids.

### Test 3: Testing for ions

Place about 10 drops of each water sample in clean test tubes or semi-micro test tubes.

Use distilled or deionised water as a control.

Test for each of the following ions.

- Chloride ion test:** Acidify the water samples with several drops of dilute nitric acid. Add several drops of 0.1 molar silver nitrate solution to each water sample as well as the control. Note the appearance of a white precipitate, which indicates the presence of chloride ions. The greater the amount of precipitate, the greater the chloride ion concentration. Rank (where possible) the water samples in terms of their relative concentrations of chloride ions.
- Sulfate ion test:** Acidify the water sample with several drops of dilute nitric acid. Add several drops of 0.1 molar barium chloride solution to each water sample as well as the control. Note the appearance of a white precipitate, which indicates the presence of sulfate ions. The greater the amount of precipitate, the greater the sulfate ion concentration. Rank (where possible) the water samples in terms of their relative concentrations of sulfate ions.
- Iron (III) ion test:** Add several drops of 0.1 molar potassium thiocyanate solution (KSCN) to each water sample as well as the control. The appearance of a red colouration indicates the presence of iron (III) ions. The deeper the red colouration, the greater the iron (III) ion concentration. Rank (where possible) the water samples in terms of their relative concentrations of iron (III) ions.
- Phosphate ion test:** Place 2–3 mL of water sample in a large test tube and add 5 mL of the ammonium molybdate–sulfuric acid reagent and 2 mL of ascorbic acid solution. Place the tube in a hot-water bath at 90°C. Repeat this procedure with a control solution containing phosphate ions. A blue colour indicates the presence of phosphate ions.

*Note:* A negative test (i.e. where no precipitate or colour change is observed) does not necessarily mean that these ions are absent from the water sample. It may mean that they are below the detectable limit of the test used.

- Sensitivity of the silver nitrate test for chloride:** Use distilled water to make 1 : 10 dilutions of the 0.1 molar sodium chloride solution supplied (i.e. 1 mL diluted to 10 mL). Use this solution to make further dilutions to produce 0.01 molar, 0.001 molar, 0.0001 molar and 0.00001 molar NaCl. Test 10 drops of each solution with 2 drops of the silver nitrate solution. At what dilution does a precipitate *not* form?

### (b) Quantitative tests

Quantitative tests are used to measure the actual amount or concentration of solutes in the water samples.

#### Test 4: Suspended solids

Choose the water sample that is the most turbid (or brackish) to conduct this test.

- Select a quantitative filter paper and weigh it on an electric balance.
- Set up a filtration apparatus and filter a known volume (e.g. 500 mL or 1 L) of the water sample through the filter paper.  
*(Note:* Keep the filtrate for Test 5.)
- Place the filter paper containing any solids on a clock glass and dry in a desiccator or low temperature oven. Allow to cool and reweigh the filter paper. Calculate the mass of solids deposited.
- Calculate the mass (in milligrams) of suspended solids per litre of water.

#### Test 5: Total dissolved solids (TDS)

Use the filtrate from Test 4.

- Measure a known volume (e.g. 300 mL to 500 mL) of the filtrate from Test 4, place it in a clean 1 litre beaker and gently evaporate and concentrate the water on a hot plate until its volume is reduced to about 50 mL. Place a clock glass over the beaker to avoid spitting. Allow the concentrated solution to cool.

# PRACTICAL ACTIVITIES

2. Weigh a clean, dry 500 mL beaker and carefully transfer the concentrated solution into it with the aid of small volumes of water from a wash bottle.
3. Evaporate the concentrated solution slowly in a low-temperature drying oven. When it is completely dry and cold, reweigh the beaker and contents.
4. Calculate the mass (in milligrams) of dissolved solids per litre of water.

## Test 6: pH

For each water sample, measure its pH using narrow range universal indicator paper or a calibrated pH probe.

Rank the water samples from most-acidic to least-acidic.

## Test 7: Chloride ion concentration

Use the seawater sample for this test.

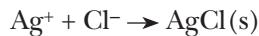
Choose one of the following methods.

### Part A. Volumetric method

1. Prepare a 1-in-5 dilution of the sea water in a 250 mL volumetric flask using a 25.00 mL pipette.
2. Fill a burette with standard 0.10 molar silver nitrate solution.
3. Pipette 25.00 mL of diluted sea water into a conical flask resting on a white square of paper. Add 5 mL of dilute nitric acid from a measuring cylinder. Use a graduated pipette to add 1.0 mL of 5% (w/v) potassium chromate indicator to the flask.
4. Titrate the salt water with constant swirling of the flask. The end-point is reached when there is a persistent faint red-brown colouration that does not disappear with swirling.
5. Repeat the procedure with 25.0 mL of a blank control (deionised water). Use this to correct your titres from Step 4.

### Calculation:

The ionic equation for the titration is:



- (a) Calculate the number of moles of silver ions added from the burette.

- (b) Calculate the chloride ion molarity in the diluted and undiluted salt water solutions.
- (c) Calculate the chloride ion concentration in the sea water in g/L.

### Part B. Gravimetric method

1. Use a graduated pipette to measure 5.0 mL of sea water into a clean 250 mL beaker.
2. Add 10 mL of 1 molar nitric acid to the beaker and 100 mL of deionised water.
3. Use a burette to slowly add about 30 mL of 0.1 molar silver nitrate to the chloride solution in the beaker until precipitation is complete. Stir constantly with a glass rod.
4. Heat the suspension to near boiling and turn off the heat. Stir constantly during the heating. Allow the silver chloride precipitate to coagulate and settle for several minutes.
5. Test the supernatant solution with a few drops of silver nitrate solution to ensure complete precipitation has occurred. Place a clock glass on the beaker and store it until the next lesson.
6. Place a quantitative filter paper in a 120°C drying oven for 15 minutes and then weigh it after cooling on an electric balance.
7. Set up the filtration apparatus and decant the supernatant solution through it. Transfer the precipitate of silver chloride quantitatively to the filter paper with the aid of a glass rod and wash bottle. Wash the precipitate with a little 0.01 molar nitric acid.
8. Place the filter paper and contents on a clock glass and heat it in a 120°C drying oven for 1 hour. Cool and reweigh the paper and precipitate. Calculate the mass of silver chloride precipitate collected.

### Calculation:

- (a) Calculate the mass of chloride ion present in the silver chloride ( $\text{AgCl}$ ) collected from the 5.0 mL of original sea water.

- (b) Calculate the concentration of chloride ions (in g/L of sea water).

(Note: Sea water typically has a chloride concentration of 19 g/L.)

# DATA ANALYSIS

## Test 8: Additional quantitative tests using data loggers and probes

Schools may have available the necessary probes and data loggers to perform the following quantitative tests on the water samples. Follow the instructions provided with the data loggers to measure the desired property.

- (a) *Turbidity*: Calibrate the turbidity probe with the standard turbidity mixture provided. Measure the turbidity of the water samples. Those samples that have turbidities greater than the supplied standard will need to be systematically diluted with deionised water.
- (b) *Conductivity*: Conductivity meters can be used to measure the TDS of a water sample as most dissolved solids are ionic. The conductivity meter needs to be calibrated first with the supplied standards; the unknown water samples can then be measured.

## Results and conclusion

Briefly describe the outcome of your investigation.

## Questions

Answer the following questions in your report on this experiment.

1. When testing for chloride ions with silver nitrate, explain why the water sample is initially acidified with nitric acid.
2. In the gravimetric determination of chloride ions, explain why the mixture is heated prior to filtration.
3. Explain why probes connected to data loggers need to be calibrated prior to use.

## 14.2 DATA ANALYSIS

### TESTING FOR HEAVY METAL POLLUTION AND EUTROPHICATION

Read the following second-hand data, and answer the questions that follow.

#### Monitoring heavy metal pollution in waterways

Environmental chemists monitor heavy metal pollution in waterways. This testing is important as heavy metals (such as lead, mercury and cadmium) become concentrated in the tissues of aquatic organisms. This concentration increases along the food chain. These metals can eventually be incorporated into human tissue when human beings eat the aquatic organisms. Sampling of waterways around Sydney has shown that there are high heavy metal levels in sediments in various bays in Sydney Harbour and the Parramatta river (e.g. Homebush Bay and Rozelle Bay). This is the result of polluted discharges from stormwater canals.

#### Cation tests for heavy metal ions

In order to perform cation tests for heavy metals in samples of environmental water, the water samples need to be concentrated sufficiently to raise the concentration to a detectable level with the reagents used. This is a laborious and time-consuming process. For example, a water sample that contains 10 mg/L (10 ppm) of lead may need to be concentrated by a factor of 20.

Heavy metals tend to form precipitates with sodium sulfide solution. This test does not distinguish which heavy metals are present.

Consider the following simplified example where a concentrated water sample is tested qualitatively for mercury, lead, cadmium, zinc and chromium ions.

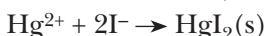
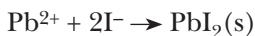
# DATA ANALYSIS

## **Test 1: Lead and mercury — testing with chloride ions in acidic solution**

To a concentrated sample of the water add drops of hydrochloric acid. A white precipitate indicates that lead and/or mercury ions are present, as they form insoluble chlorides.

### *Confirmation:*

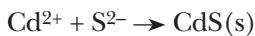
Filter and wash the white precipitate. Keep the filtrate for Test 2. Dissolve the precipitate in a little hot water. Add drops of potassium iodide solution. A bright yellow precipitate confirms lead ions and a red precipitate confirms mercury (II) ions.



Alternatively, add drops of sodium hydroxide solution to the solution. A yellow or red precipitate of  $\text{HgO}$  indicates mercury. A white precipitate,  $\text{Pb(OH)}_2$ , indicates lead.

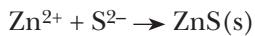
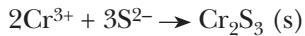
## **Test 2: Cadmium — testing with sulfide ions in acidic solution**

Use the acidic filtrate from Test 1. Add drops of sodium sulfide solution until no further precipitation occurs under acid conditions. A yellow precipitate ( $\text{CdS}$ ) indicates that cadmium ions are present.



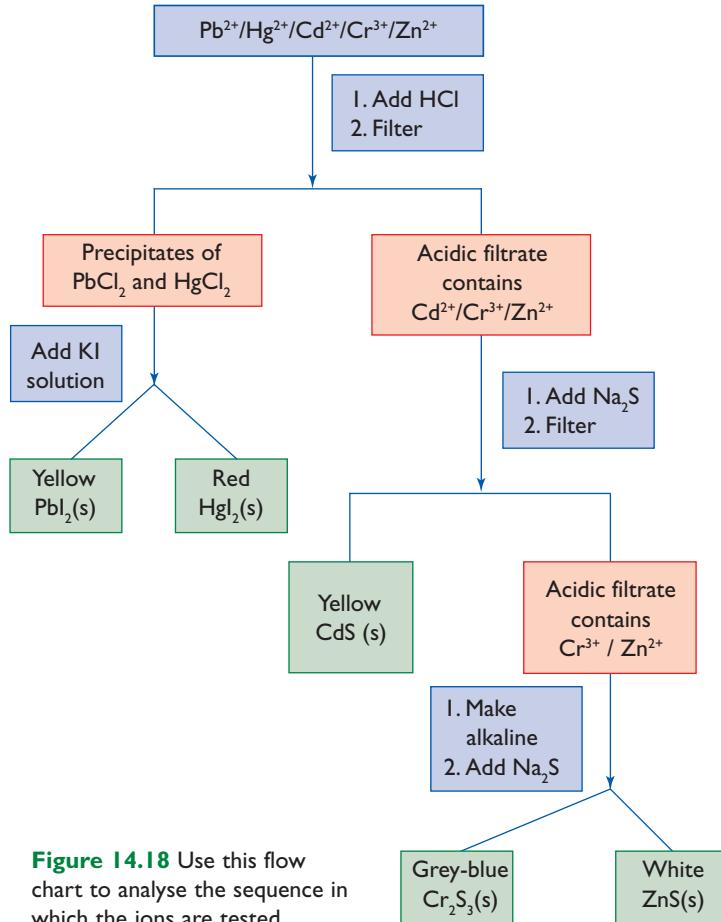
## **Test 3: Zinc and chromium — testing with sulfide ions in alkaline solution**

Filter off the precipitate from Test 2 and then make the filtrate weakly alkaline with a minimum of sodium hydroxide. Add sodium sulfide solution. A grey-blue precipitate indicates chromium ions, and a white precipitate indicates zinc ions.



### *Confirmation:*

If excess NaOH was added in Test 3, then a grey-blue chromium hydroxide precipitate will initially form and then dissolve in excess to form a green solution. In the case of zinc ions, a white zinc hydroxide precipitate forms with continued addition of NaOH and this precipitate dissolves to give a colourless solution with excess NaOH.



**Figure 14.18** Use this flow chart to analyse the sequence in which the ions are tested.

## **Instrumental tests for heavy metal ions**

Rapid on-site measurements of heavy metals in waterways can be achieved by using ion-selective electrodes (ISE). ISEs may suffer, however, from interference from other ions. The primary methods of analysing for heavy metals in water samples are flame atomic absorption spectroscopy (FAAS), graphite furnace (GFAAS), anode stripping voltammetry (ASV), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and X-ray fluorescence spectroscopy (XRFS). In the future, the primary method that will be used is inductively coupled plasma mass spectroscopy (ICP-MS) as this technique is many orders of magnitude more sensitive than other common methods currently used. Consider the following detection limits using three of these methods.

# DATA ANALYSIS

Heavy metal	Detection limits (parts per billion)		
	GFAAS	FAAS	ICP-MS
cadmium	2	0.2	0.05
lead	30	1	0.05

In Western countries, the typically natural range for lead levels in ground and surface water is between 5 and 30 ppb. In Australia, lead levels should not exceed 10 ppb for potable water. FAAS cannot detect such low lead levels and so GFAAS is more suitable for such analyses. The combination of corrosive water, lead-soldered joints or brassware that contains small amounts of lead in houses can result in drinking water that contains unhealthy levels of lead. The maximum levels of other heavy metals in potable water are set at 2 ppb for mercury and 5 ppb for cadmium.

## Questions

- Explain why instrumental methods for the determination of heavy metals in water are superior to traditional gravimetric methods.
- A sample of polluted water contains either lead ions or mercury ions. Describe simple cation tests to determine which ion is present.
- A sample of water contains mercury and cadmium ions. Explain why the mercury ions must be removed before the cation test for cadmium is performed.
- Explain why GFAAS rather than FAAS is used to determine low lead levels in water.

## Monitoring eutrophication in waterways

The excessive growth of cyanobacteria, algae and water weeds has often become a major problem in NSW lakes and rivers. The term ‘algal bloom’ is commonly used to describe the green colouration that develops in such waterways as a result of this excessive growth. Algal blooms result from water that is polluted with excessive amounts of nitrogen and phosphorus nutrients from sources such as farm water run-off containing fertilisers and effluent water from sewage treatment works. Laundry detergent often contains phosphates and this effluent makes its way into the sewerage system.

The term *eutrophication* describes this enrichment of waterways with excessive nutrients that leads to abundant algal growth.

The presence of algal blooms has several effects.

- Sunlight is blocked by excessive plant growth at the water surface. Light cannot penetrate deeper into the water to allow deeper producers to photosynthesise.
- Algal blooms interfere with diffusion of oxygen from the air into the water.
- On the death of the algae the dissolved oxygen levels in the water become severely depleted as aerobic decomposers break down their remains. This is detrimental to other organisms in the water.
- Once the DO levels drop to near zero anaerobic decomposers become active and foul smelling gases are released in the stagnant water.

Following extensive research into the nitrogen and phosphorus requirements of various water plants including algae, chemists have developed guidelines for the protection of aquatic ecosystems from eutrophication. In recent years these guidelines have become more stringent. The Australian and New Zealand Environment and Conservation Council (ANZECC) in 2002 recommended the following maximum levels in lakes and (raw water) storage reservoirs.

- phosphorus = 10 ppb
- nitrogen = 350 ppb

In 2005, measurements of the water in the Warragamba storage reservoir showed the total phosphorus to be 5 ppb and the total nitrogen to be 250 ppb. ANZECC makes other recommendations for levels of phosphorus and nitrogen in estuarine, coastal and river systems. For example, the recommended maximum phosphorus content of rivers and streams is about twice as great as the recommended levels for lakes.

The above data shows that the levels of phosphorus must be lower than the levels of nitrogen in our waterways if eutrophication is to be avoided. Phosphorus levels seem to be the limiting factor controlling plant growth in many aquatic systems. It has been shown in a number of studies that *visible eutrophication* occurs

# DATA ANALYSIS

when the total nitrogen level exceeds 400–600 ppm and/or the total phosphorus level exceeds 40–60 ppm. These levels are often expressed as an N:P ratio. The N and P ranges shown above correspond to an N:P ratio of 10:1. Although N:P ratios greater than 10:1 tend to protect waterways from eutrophication, the situation is more complex as cyanobacteria can grow very well in water that is rich in nitrogenous nutrients and very poor in phosphorus. Adherence to the ANZECC guidelines is the best way to avoid eutrophication.

Total nitrogen and total phosphorus can be measured in a number of ways. Most dissolved nitrogen is ultimately oxidised in natural systems to produce nitrate ions. Some nitrogen is present in organic compounds. Most dissolved phosphorus is in the form of phosphate ions. Some phosphorus exists as organic phosphorus.

## Measuring nitrogen

The Kjeldahl method is a procedure used to measure the organic nitrogen of a water sample. This procedure involves the conversion of all the nitrogen in a sample to ammonia which is then measured by titrating with standard acid.

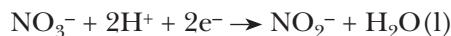
Conversion of organic nitrogen to ammonia:



Titration:  $2\text{NH}_3(\text{aq}) + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4$

The soluble nitrate content of a water sample can be determined instrumentally using a colourimeter. The nitrate ions are reacted with a reductant to convert them to nitrite ions. The nitrite reacts with a colour reagent to produce a pink-purple azo-dye that is measured colourimetrically against known standards. The colourimetric method for measuring nitrate is typically used for concentrations of these ions in the range from 2 ppm (2000 ppb) down to about 0.020 ppm (20 ppb).

Reduction of nitrate to nitrite:



Formation of azo-dye:



## Measuring phosphorus

The phosphorus content of a water sample is also measured colourimetrically by oxidising the phosphorus to phosphate and reacting the phosphate ions with molybdate ions and ascorbic acid to form a blue molybdenum–phosphate complex. These methods of measuring the nitrogen and phosphorus content allow chemists to detect quite low levels of these elements in water. The colourimetric method for measuring phosphate ions is typically used for concentrations of these ions in the range from 3 ppm (3000 ppb) down to about 0.010 ppm (10 ppb).

Oxidation of phosphorus compounds to phosphate:  $(\text{P})_{\text{Compounds}} \rightarrow \text{PO}_4^{3-}$

Formation of molybdate dye:



## Questions

- Describe the possible consequences of eutrophication of a waterway.
- Explain why ANZECC has set guidelines for the maximum levels of nitrogen and phosphorus in waterways.
- Explain briefly the method of determining the nitrogen and phosphorus levels in river water.
- The water from a river was tested for eutrophication by determining the nitrogen and phosphorus content. The results were:  
 $N = 0.50 \text{ ppm}$        $P = 0.025 \text{ ppm}$

Evaluate these results.

# DATA ANALYSIS

## 14.3 DATA ANALYSIS

### INVESTIGATING THE SYDNEY WATER SUPPLY

Read the following text, and answer the questions that follow.

#### The catchment area

Five major systems form the Sydney catchment that covers over 16 000 square kilometres to the south and west of Sydney. These are the Warragamba system, the Upper Nepean system, the Woronora system, the Blue Mountains system and the Shoalhaven system. Each system contains:

- rivers, lakes, dams and reservoirs
- pumping stations, water filtration plants and pipelines.

#### Questions

Use the key to the map (page 354) to answer the following questions.

1. Lake Burragorang is a huge reservoir formed behind Sydney's largest dam. Identify this dam.
2. Identify two of the major sources of raw water for the Prospect water filtration plant (WFP).
3. Name the zone(s) that are supplied with potable water from the Prospect WFP.
4. The Shoalhaven system was designed to be used in times of drought.
  - (a) Identify the other important purpose of the Shoalhaven system.
  - (b) When required, water from the Shoalhaven can be transferred to the Warragamba or Upper Nepean systems. Identify the ways in which water can be transferred.
5. Identify the water filtration plants that can supply potable water to the Penrith area in Sydney's west.

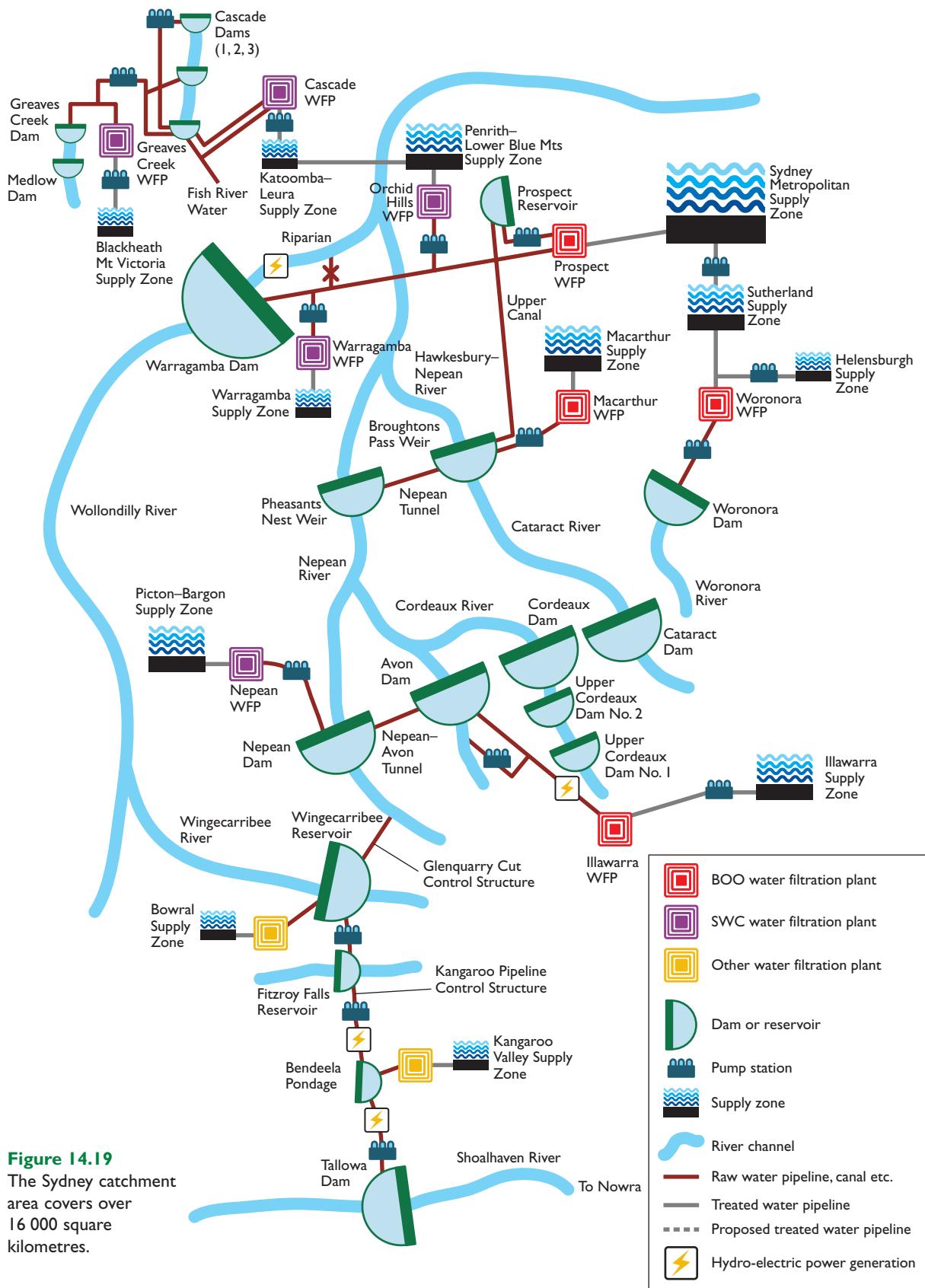
#### Contamination in the catchment

##### Sources of contamination

Various factors lead to contamination of the catchment water. For the Sydney catchment these include the following.

- *Turbidity*: Surface water run-off into rivers from bushland and grazing land in the catchment after heavy rain leads to temporary increases in turbidity and nutrient levels of the water.
- *High levels of iron and manganese*: The catchment area for Woronora Dam as well as the Avon and Cordeaux Dams has high natural iron and manganese levels that have leached from the local soil and rock strata. This leads to water that is coloured and has a metallic taste.
- *Treated/untreated sewage effluent*: Sewage treatment plants along some of the catchment rivers discharge treated sewage into the river. These treatment plants are usually far enough upstream that little phosphorus and nitrogen contamination is usually detected near the dam walls. Some areas near Lake Burragorang remain connected to septic tanks. Raw sewage overflow, which can occur at various times, does have adverse effects on water quality in Werriberri Creek and Lake Burragorang.
- *Microbes*: The catchment water contains variable levels of microbes including cyanobacteria, coliform bacteria as well as cysts of parasites such as *Cryptosporidium* and *Giardia*. Water run-off from agricultural land contributes to this problem.
- *Pesticides*: Low levels of organochlorine and organophosphate pesticides have been detected in the outer catchment. These pesticides come from agricultural properties.
- *Mining*: Zinc, copper and lead have been detected in areas near abandoned mines (e.g. Yerranderrie). Rehabilitation work is undertaken where sources of heavy metals are identified. Coal mining in the outer catchment also poses a threat to water quality.
- *Grazing*: Cattle graze extensively along the creeks and rivers in the catchment. Cattle faecal matter is carried into creeks and rivers during storms.
- *Native and feral animals*: These animals are potential carriers of parasites. These parasites can find their way into surface water or creek water.

# DATA ANALYSIS



**Figure 14.19**

The Sydney catchment area covers over 16 000 square kilometres.

# DATA ANALYSIS

## Chemical tests for contaminants

Tests for water contaminants can be classified as physical, biological or chemical. In this section we examine some of the common chemical tests that can be performed by an analytical chemist.

### Contamination with acids and alkalis

Hydrogen ions or hydroxide ions can contaminate water supplies. This process can be natural or due to human activity (e.g. mining). The pH of potable water should be between 6.5 and 8.5. If the water is too acidic, it can result in pipe corrosion. If it is too alkaline it will taste bitter and produce scaling in pipes. The pH can be measured using a pH meter or by using narrow-range indicator papers.

### Contamination with metal ions

Various cations can contaminate water supplies. The presence of calcium and/or magnesium ions can produce hard water. Hard water will not lather with soap, and so needs to be softened. The total hardness can be chemically measured using an EDTA titration using a suitable indicator (e.g. Eriochrome Black-T). The mole stoichiometry is 1:1 (metal ion: EDTA). The hardness is typically expressed as mg/L of  $\text{CaCO}_3$ . Heavy metal ions can contaminate water supplies in water draining from mining sites or from factory effluents. The level of this contamination can be determined using AAS.

### Contamination with salt

Rising watertables can result in salt contamination. The removal of trees from farming land is one major cause of salinity. The concentration of sodium ions, chloride ions and sulfate ions will increase as salinity levels rise. The concentration of sodium ions can be readily determined using AAS or flame photometry. Chloride ions and sulfate ions can be determined volumetrically or gravimetrically. For example, the concentration of chloride ions can be determined by titration with standard silver ions using a chromate indicator.

### Contamination with nitrogen and phosphorus

Agricultural water can find its way into the local catchment and this will lead to increases in nitrogen and phosphorus levels.

The soluble nitrate content of a water sample can be determined instrumentally using a colourimeter. The nitrate ions are reacted with a reductant to convert them to nitrite ions.

The nitrite reacts with a colour reagent to produce a pink-purple azo-dye that is measured colourimetrically against known standards.

The phosphorus content of a water sample is also measured colourimetrically by oxidising the phosphorus to phosphate and reacting the phosphate ions with molybdate ions and ascorbic acid to form a blue molybdenum-phosphate complex.

## Questions

6. Parasites such as *Giardia* have sometimes contaminated the Sydney water catchment. Describe the source of this type of contamination.
7. A sample of water has a metallic taste. Identify a likely contaminant that would produce this metallic taste.
8. High zinc levels are measured in a creek within the Sydney Catchment. Identify a possible source of such contamination.
9. In the outer catchment, sewage is sometimes allowed to overflow at designated points to prevent sewage backing up into houses. Identify the likely problems on the water supply associated with this practice.
10. A sample of water from Lake Burragorang is treated in the water filtration plant. The pH is 5.8. Explain how the pH will be adjusted to acceptable levels.
11. A creek has become contaminated by rising salinity in the soil. The sulfate concentration of a water sample was determined colourimetrically. The water sample was diluted by a factor of 10 and the diluted sample was treated with barium chloroanilate reagent to produce a yellow-coloured ion whose concentration was directly proportional to the sulfate concentration. The colour intensity (absorbance) was compared with a series of calibration standards. The results are tabulated below.

# DATA ANALYSIS

Sulfate concentration (ppm)	100	200	300	400	Diluted unknown
Absorbance	0.10	0.20	0.30	0.40	0.12

- (a) Plot a calibration graph.
- (b) Determine the sulfate concentration in the undiluted water sample from the creek.
- (c) NHMRC guidelines suggest a maximum level of 400 ppm for sulfate in potable water. Determine whether the water needs to be treated.
- (d) Describe a qualitative laboratory test to confirm the presence of sulfate ions in the creek water.

## Purifying water

Water treatment plants use both physical and chemical processes to produce potable water from the raw dam water.

### Physical treatments

The physical processes that were discussed previously are listed below. Refer to the previous text sections for more detail.

- (a) Screening out large debris
- (b) Coagulation to increase particle size
- (c) Sedimentation to remove larger suspended particles
- (d) Filtration to remove finer suspended particles.

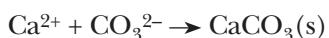
### Chemical additives and chemical processes

The chemical processes that were discussed in previous text sections are listed below. Refer to the previous text sections for more detail.

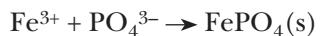
- (a) Aeration to oxidise soluble iron and manganese salts to insoluble compounds
- (b) Oxidation (e.g. by potassium permanganate) of iron and manganese salts; e.g.



- (c) Lime softening to precipitate out high levels of calcium and magnesium ions; e.g.



- (d) Calcium hydroxide addition to raise the pH in the coagulation tank
- (e) Addition of iron (III) chloride to precipitate phosphate ions in the coagulation tank; e.g.



- (f) pH adjustment in post-treatment
- (g) Addition of chlorine and ammonia to kill microbes (biochemical)
- (h) Addition of fluoride ions to assist in tooth decay prevention (biochemical).

### Questions

12. Classify the following purification processes as physical or chemical.
  - (a) Addition of calcium oxide and sodium carbonate
  - (b) Screening
  - (c) Sedimentation
  - (d) Addition of potassium permanganate
13. When iron (III) chloride is added to water, it hydrolyses to produce iron (III) hydroxide.
  - (a) Write a balanced equation for this reaction.
  - (b) Explain the purpose of the iron (III) hydroxide that is formed.
14. The main disinfecting agent for treating water is hypochlorous acid ( $\text{HOCl}$ ) which forms when chlorine is dissolved in water.
  - (a) Write a balanced equilibrium equation for this reaction.
  - (b) Hypochlorous acid can also be generated by adding sodium hypochlorite to water. This method is used in plants closer to cities. Write a balanced equilibrium equation for this reaction.
15. To ensure that disinfection continues as water moves through the pipelines, ammonia is added to produce monochloramine ( $\text{NH}_2\text{Cl}$ ). Write a balanced equation for the formation of monochloramine by the reaction between ammonia and hypochlorous acid.
16. Sodium silicon fluoride ( $\text{Na}_2\text{SiF}_6$ ) is one compound that can be added to water to increase the level of fluoride ions. It hydrolyses in water to produce an acidic solution of fluoride ions. Silicon dioxide also precipitates in this hydrolysis reaction. Write a whole formula balanced equation for this hydrolysis reaction.