

Chapter

12 *ANALYTICAL CHEMIST*



Figure 12.1

Analytical chemists use a variety of traditional gravimetric and volumetric techniques as well as instrumental techniques.

Introduction

A wide variety of chemical, pharmaceutical and food production companies employ analytical chemists. An important aspect of their work is quality control. Analytical chemists are often employed as environmental chemists. In this role they are involved in monitoring water and air quality to ensure that the environment does not become contaminated with pollutants. Analytical chemists utilise a wide range of chemical and instrumental techniques.

In this chapter

- | | | |
|------|------------------------|----------|
| 12.1 | Identification of ions | page 260 |
| 12.2 | Instrumental analysis | page 271 |

12.1 IDENTIFICATION OF IONS

Remember

Before beginning this section, you should be able to:

- identify some combinations of solutions that will produce precipitates, using solubility data
- construct ionic equations to represent the dissolution and precipitation of ionic compounds in water
- present information in balanced chemical equations and identify the appropriate phase descriptors (s), (l), (g) and (aq) for all chemical species.

Key content

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

- deduce the ions present in a sample from the results of tests
- perform first-hand investigations to carry out a range of tests, including flame tests, to identify the following ions: phosphate, sulfate, carbonate, chloride barium, calcium, lead, copper, iron
- identify data, plan, select equipment and perform first-hand investigations to measure the sulfate content of lawn fertiliser and explain the chemistry involved
- analyse information to evaluate the reliability of the results of the above investigation and to propose solutions to problems encountered in the procedure.

cation: a positively charged ion

anion: a negatively charged ion

reagent: a substance or solution that causes a reaction to occur

confirmation test: additional tests used to confirm the original analysis

Anion analysis

Many analytical chemists analyse materials for the presence of specific **cations** and **anions**. In this section we shall investigate the traditional chemical tests that an analytical chemist could use to identify various anions in solution.

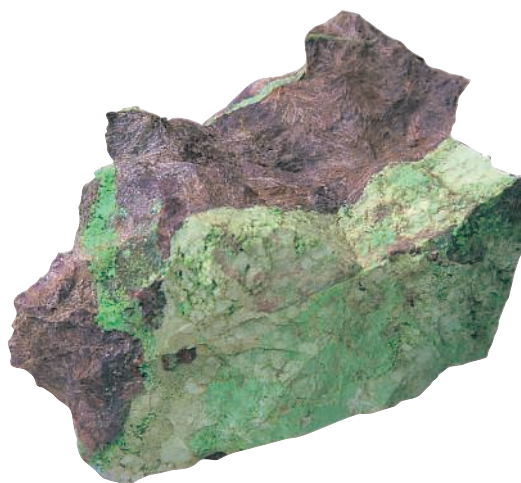


Figure 12.2 Nickel carbonate is a green mineral. Some minerals of copper and chromium are also green. An analytical chemist uses a knowledge of the colour of compounds, as well as other chemical tests, to identify the metal present in a mineral.

The following anions will be investigated:



Anions can be identified and distinguished using a variety of simple qualitative tests involving the formation of gases or precipitates. Different procedural steps are used depending on whether there is only one anion, or a mixture of anions, present. Normally, a series of elimination tests is conducted in a strict order. This is important because with some **reagents**, different ions can produce similar results.

Once an ion has been identified, additional **confirmation tests** may also be carried out. You should remember some important solubility rules from *Chemistry 1 Preliminary Course*. These include:

- all nitrate salts are soluble — so adding nitric acid will not cause precipitation of cations
- all Group I salts are soluble — so solutions of sodium and potassium ions will not cause the precipitation of anions.

Table 12.1 provides a summary of some useful solubility information that will help you in your analysis of ions in mixtures.

Table 12.1 Solubility rules

Anion	Soluble	Slightly soluble	Insoluble
CO_3^{2-}	$\text{Na}^+, \text{K}^+, \text{NH}_4^+$	—	most
Cl^-	most	Pb^{2+}	Ag^+
OH^-	$\text{Na}^+, \text{K}^+, \text{NH}_4^+, \text{Ba}^{2+}$	Ca^{2+}	most
PO_4^{3-}	$\text{Na}^+, \text{K}^+, \text{NH}_4^+$	—	most
SO_4^{2-}	most	$\text{Ca}^{2+}, \text{Ag}^+$	$\text{Ba}^{2+}, \text{Pb}^{2+}$

Anion elimination tests

Table 12.2 lists the common tests used in a chemical laboratory to identify a selection of anions. The tests for ‘unknown’ solutions should be performed in the listed order to avoid invalid conclusions. This order is called an *elimination* sequence. The anion solutions to be tested should have a minimum concentration of 0.1 molar. Normally 1–2 mL samples of the unknown solution are placed in separate clean test tubes for testing.

If unknown solutions contain more than one anion, the first anion identified by the elimination sequence must be removed (e.g. by filtration of the precipitate formed) before the next tests are conducted.

Table 12.2 Anion analysis: elimination sequence

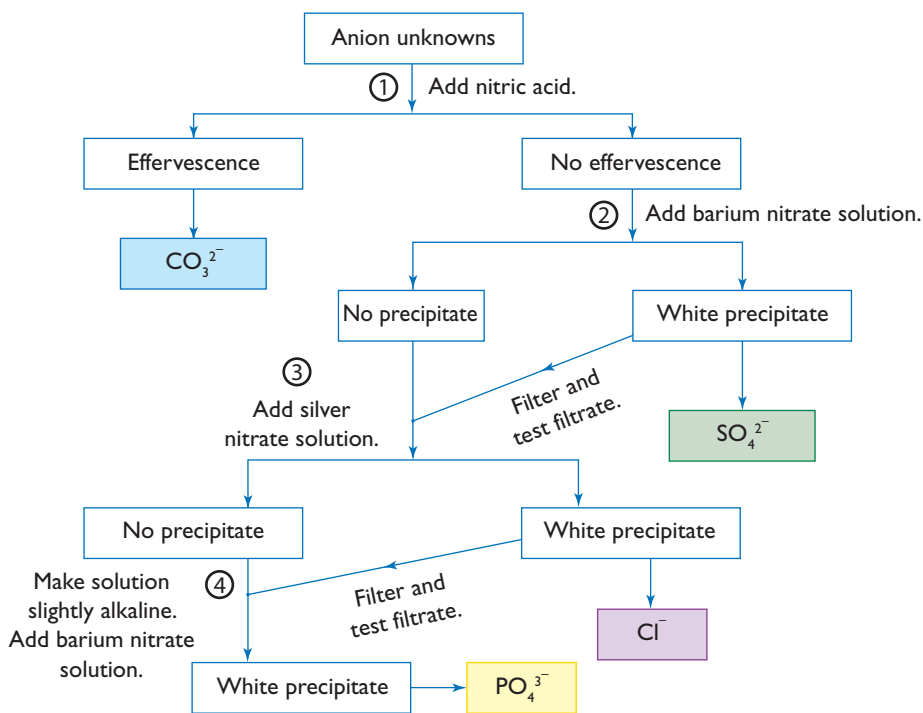
Anion	Procedure	Observation/conclusion
	A. Add 2 mol/L nitric acid dropwise into the original unknown solution.	A. An effervescence of a colourless gas (CO_2) indicates a carbonate. Use limewater to confirm carbon dioxide is evolved. $\text{CO}_3^{2-} + 2\text{H}^+ \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
	B. Confirmation test: Test <i>original</i> solution with universal pH paper.	B. Solution has a pH in the alkaline range (8–11). $\text{CO}_3^{2-} + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$
SO_4^{2-}	A. Acidify the unknown solution with a little nitric acid (to remove any carbonate from the previous step) and add drops of a dilute solution of barium nitrate.	A. A white precipitate of barium sulfate indicates sulfate ions are present. $\text{SO}_4^{2-} + \text{Ba}^{2+} \rightarrow \text{BaSO}_4(\text{s})$
	B. Confirmation test: To the acidified solution add drops of lead (II) nitrate solution.	B. A white lead (II) sulfate precipitate forms. $\text{SO}_4^{2-} + \text{Pb}^{2+} \rightarrow \text{PbSO}_4(\text{s})$
Cl^-	A. Acidify the original unknown solution (or filtered solution from the previous step) with a few drops of dilute nitric acid. Add drops of silver nitrate solution.	A. A white precipitate of silver chloride indicates chloride ions are present. $\text{Cl}^- + \text{Ag}^+ \rightarrow \text{AgCl}(\text{s})$
	B. Confirmation test: Add 1–2 mL of 10% ammonia solution to the suspension and heat in a water bath.	B. The white precipitate should dissolve to form a colourless silver complex ion. $\text{AgCl}(\text{s}) + 2\text{NH}_3 \rightarrow \text{Ag}(\text{NH}_3)_2^+ + \text{Cl}^-$
PO_4^{3-}	A. Make the original unknown solution (or the filtered solution from the previous step) slightly alkaline (pH ~10) with drops of ammonia solution. Add dropwise a solution of barium nitrate.	A. A white precipitate forming in the slightly alkaline solution indicates the presence of phosphate ions. $2\text{PO}_4^{3-} + 3\text{Ba}^{2+} \rightarrow \text{Ba}_3(\text{PO}_4)_2(\text{s})$

Table 12.2 Continued

Anion	Procedure	Observation/Conclusion
	<p>B. Confirmation tests:</p> <ol style="list-style-type: none"> 1. Add ammonium molybdate solution to the acidified unknown solution. Warm the mixture gently. 2. Acidify the solution with 5 mol/L sulfuric acid. Add ammonium molybdate and ascorbic acid. Heat to 90°C in a water bath. 	<p>B. 1. A yellow precipitate of ammonium phosphomolybdate forms.</p> <p>$(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 3\text{H}_2\text{O}$</p> <p>2. A blue complex (called <i>molybdenum blue</i>) forms. The intensity of colour of the blue complex is proportional to the phosphate concentration.</p>

Figure 12.3

The anion elimination sequence flow chart summarises the steps that are followed to identify and distinguish between anions.



TESTING FOR CHLORIDE IONS

SAMPLE PROBLEM 12.1

SOLUTION

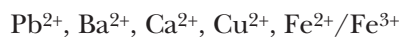
A mixed solution was prepared by dissolving potassium chloride and sodium sulfate in water. Explain how a student could show experimentally that both chloride ions and sulfate ions were present in the solution.

Take a sample of the solution in a test tube and acidify it with a few drops of nitric acid. This acidification creates an environment in which only certain compounds will precipitate. Now add excess drops of barium nitrate solution until no further precipitation occurs. A heavy white precipitate indicates that sulfate ions are present. Barium sulfate is very insoluble in water.

Filter the mixture from the first reaction and keep the acidic filtrate. Now add drops of silver nitrate solution. A white precipitate of silver chloride should form. This indicates that chloride ions are present. The tests should be done in this order to avoid the possibility of precipitation of sparingly soluble silver sulfate.

Cation analysis

The following cations will be investigated:



Colour of solution

In aqueous solution many cations are colourless. Table 12.3 shows the distinctive colours of some cations.

Table 12.3 Colours of some hydrated cations

Hydrated cation	Solution colour
Fe^{3+}	yellow-orange to pale yellow
Fe^{2+}	pale green to colourless
Cu^{2+}	blue to green-blue

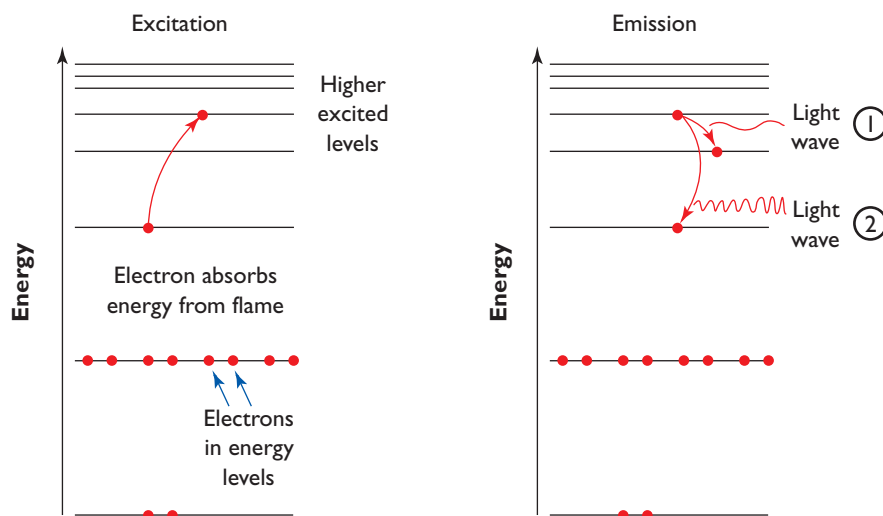
Flame tests

flame test: a test that can be used to distinguish some cations by the colour their salts impart to a flame (such as a blue Bunsen flame)

Many metal ions produce characteristic colours when their salts are volatilised in a blue (non-luminous) Bunsen flame (called a **flame test**). You will have already observed these flame colours in firework displays. Chloride salts of various cations work best.

Some metal ions produce characteristic flame colours. The explanation for this observation lies in the electron shell structure of the atom. When a metal salt is vapourised in a flame, the outer shell electrons of the metal ion may absorb energy and move to higher 'excited' energy levels. Excited electrons are unstable and as they fall back to lower levels they emit light of various characteristic frequencies. Some of these frequencies correspond to the visible region of the electromagnetic spectrum. We see the result of the emission of these coloured photons. Figure 12.4 shows this process of excitation and emission.

Figure 12.4
Electrons can absorb a quantum of energy and move into an excited energy level. The electron can then drop back to slower energy level with the emission of photons of light of different frequencies.



There are several procedures that can be used.

- Dip a platinum wire into concentrated hydrochloric acid to clean it. Heat the wire to remove any impurities. Dip the wire again into the acid and then into the powdered salt which sticks to the film of acid on the wire. Volatile chlorides of the metal ions are produced when the wire is heated in the flame.
- Dissolve the chloride salts in water and spray the resulting solution into the blue Bunsen flame using an atomiser.

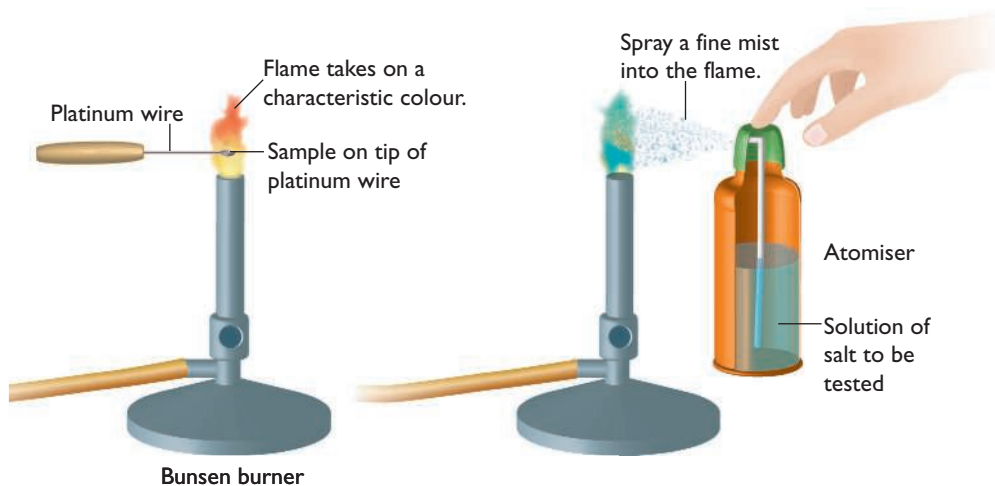


Figure 12.5

Various metal ions produce characteristic colours when they are volatilised in a flame.

Table 12.4 Flame colours

Cation	Flame colour
calcium	brick red
barium	yellow-green (apple green)
copper	green
sodium	yellow
strontium	scarlet

Table 12.4 shows the flame colours of some metallic ions. Many chemicals are contaminated with sodium ions. As sodium has a strong yellow colour in a flame, it may mask the colour of the unknown metal. Flame tests are very useful in distinguishing between calcium and barium ions because these ions are often difficult to distinguish using other chemical tests. Flame tests are commonly used as confirmatory tests rather than primary tests, as interference may occur due to the presence of other cations.

Cation elimination tests

In order to determine which cation may be present in an unknown solution, a series of elimination tests is conducted. These elimination tests are based on the formation of precipitates in solutions of varying pH. Table 12.5 lists these elimination tests for the identification of the selected cations.

The cation solutions to be tested should have a *minimum concentration* of 0.1 molar. Normally, 1–2 mL samples of the unknown solution are placed in separate clean test tubes for testing. If unknown solutions contain more than one cation, the ion that is first identified must be removed (e.g. by filtration of its precipitate) before subsequent tests are performed.

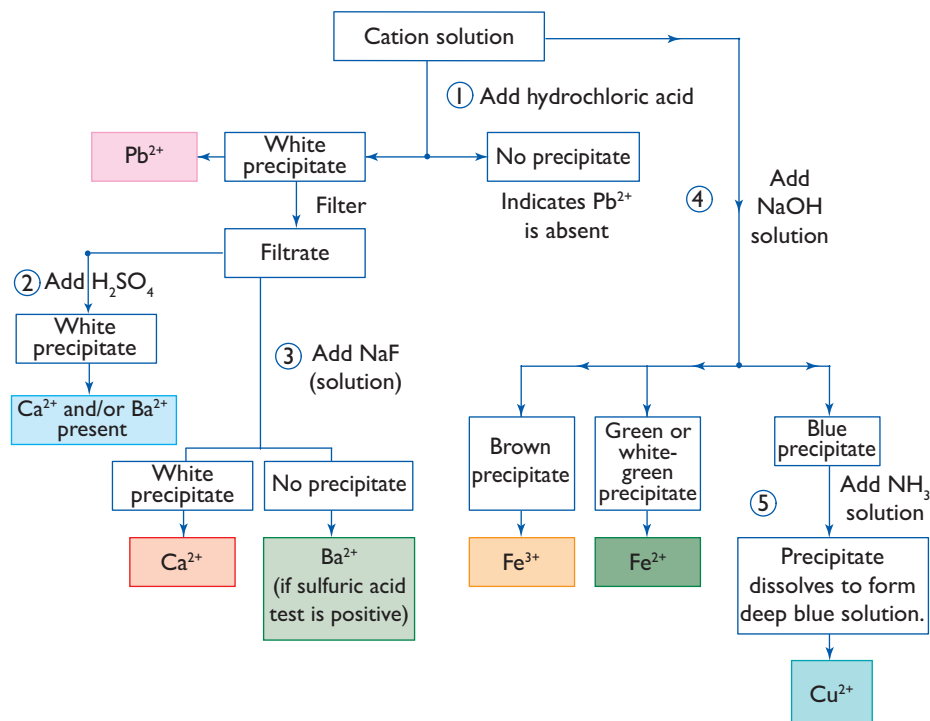


Figure 12.6

The cation elimination sequence flow chart allows a chemist to identify an unknown cation from a given set.

Table 12.5 Elimination tests for cations

Cations	Procedure	Observation/conclusion
Pb ²⁺	<p>A. Add 5 drops of dilute hydrochloric acid to the unknown solution.</p> <p>B. Confirmatory test: To the original solution add drops of dilute sodium iodide solution.</p>	<p>A. A (faint) white precipitate indicates lead ions. $\text{Pb}^{2+} + 2\text{Cl}^- \rightarrow \text{PbCl}_2(\text{s})$ Lead (II) chloride is soluble in hot water but slightly soluble in cold water.</p> <p>B. A yellow precipitate confirms that lead ions are present. $\text{Pb}^{2+} + 2\text{I}^- \rightarrow \text{PbI}_2(\text{s})$</p>
Ba ²⁺ , Ca ²⁺	<p>A. To a fresh sample of the solution (or filtered solution from the previous step) add 5–10 drops of 1 mol/L sulfuric acid solution.</p> <p>B. Confirmatory tests: (a) To a fresh sample of the solution add, dropwise, a solution of sodium fluoride (b) Use the original solid or the solution to conduct a flame test.</p>	<p>A. A white precipitate indicates either calcium or barium ions are present. Calcium sulfate may not precipitate if the solutions are too dilute. $\text{Ca}^{2+} + \text{SO}_4^{2-} \rightarrow \text{CaSO}_4(\text{s})$ $\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4(\text{s})$</p> <p>B. (a) A white precipitate confirms calcium. No precipitate suggests barium. $\text{Ca}^{2+} + 2\text{F}^- \rightarrow \text{CaF}_2(\text{s})$ (b) Brick-red flame indicates calcium ions. Yellow-green flame indicates barium ions.</p>
Cu ²⁺	<p>A. To a fresh sample of the solution add drops of 1 mol/L NaOH. Once a precipitate forms, add ammonia solution.</p> <p>B. Confirmatory test: Use the original solid or solution to conduct a flame test.</p>	<p>A. A blue precipitate forms from an original blue or green solution. The precipitate dissolves in excess ammonia to form a deep blue solution containing a copper complex ion. $\text{Cu}^{2+} + 2\text{OH}^- \rightarrow \text{Cu}(\text{OH})_2(\text{s})$ $\text{Cu}(\text{OH})_2(\text{s}) + 4\text{NH}_3 \rightarrow \text{Cu}(\text{NH}_3)_4^{2+} + 2\text{OH}^-$</p> <p>B. Green flame indicates copper ions.</p>
Fe ²⁺ , Fe ³⁺	<p>A. To a fresh sample of the original solution add drops of 1 mol/L NaOH.</p> <p>B. Confirmatory tests: To a fresh sample of the original solution add 10 drops of 4 mol/L HCl solution. (a) Remove two drops of this solution to a white tile and add a drop of potassium hexacyanoferrate(III) reagent. (b) To two other drops on a white tile add a drop of potassium thiocyanate reagent.</p>	<p>A. A brown precipitate indicates Fe³⁺. $\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe}(\text{OH})_3(\text{s})$ $\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2(\text{s})$ A green (or white green) precipitate indicates Fe²⁺. It may turn rapidly brown.</p> <p>B. (a) A dark blue colour indicates Fe²⁺. $3\text{Fe}^{2+} + 2\text{Fe}(\text{CN})_6^{3-} \rightarrow \text{Fe}_3(\text{Fe}(\text{CN})_6)_2$ (b) A deep blood-red colour indicates Fe³⁺. $\text{Fe}^{3+} + \text{SCN}^- \rightarrow \text{FeSCN}^{2+}$</p>



**TESTING FOR
LEAD IONS**

SAMPLE PROBLEM 12.2

The following experimental data was collected for an unknown solid (X). Process this information and identify the compound. Justify your conclusions with appropriate equations.

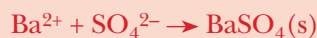
Data collected

1. Yellow-orange crystalline solid
2. Readily soluble in water
3. Aqueous solution of X is yellow
4. *Anion elimination tests:*
 - (a) Solution does not bubble when dilute nitric acid is added.
 - (b) White precipitate forms when dilute barium nitrate solution is added to the acidified yellow solution.
5. *Cation elimination tests:*
 - (a) No precipitate forms when hydrochloric acid is added to the yellow solution.
 - (b) No precipitate forms when sulfuric acid is added to the yellow solution.
 - (c) Brown precipitate forms when sodium hydroxide solution is added to the yellow solution.
 - (d) A deep red colour forms when potassium thiocyanate is added to the yellow solution.

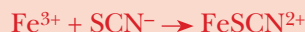
SOLUTION

The compound is iron (III) sulfate.

The anion tests show no carbonate is present but sulfate is present, because a white precipitate forms when barium ions are added.



The cation tests show that lead ions are not present as there is no precipitate with chloride ions. Calcium and barium ions are ruled out as there is no precipitate with sulfuric acid. The brown precipitate formed when NaOH is added suggests iron (III) ions. This is confirmed with the red thiocyanate test.



12.1 PRACTICAL ACTIVITIES

Identification of ions



Volumetric analysis has been considered in HSC Module 2 *The acidic environment*. Instrumental analysis will be investigated in a later section of this module.

Quantitative analysis

Chemists use a variety of techniques to determine the amount or concentration of an element, ion or compound in a sample of material. These techniques include:

- gravimetric analysis—this involves weighing materials and determining the percentage composition (by weight) of elements in compounds or components of a mixture
- volumetric analysis—this involves measuring the volume of solutions that react with other solutions of known concentration
- instrumental analysis—this involves the use of special instruments that can determine the concentration or amount of a material by measuring a property of the material (e.g. pH, colour, absorbance of light).

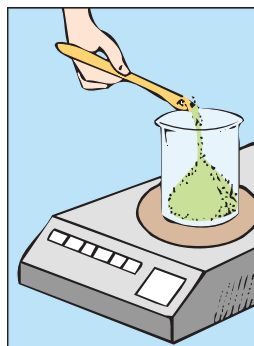
Let us examine an example of gravimetric analysis.

Figure 12.7

Gravimetric analysis often involves some of the steps shown in the diagram. A precipitate can be filtered under gravity, or by using a water suction pump connected to a side arm flask and Buchner funnel.

Gravimetric analysis

Gravimetric analysis often involves the use of precipitation reactions. When an analytical chemist is required to determine the percentage of a particular ion in an ionic compound, gravimetric analysis may be a suitable choice. Let us look at a simple case in the following worked example.



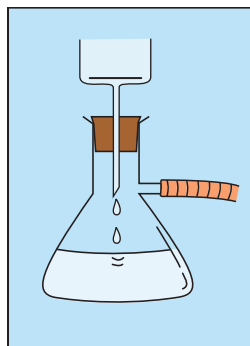
(a) Weighing the sample to be analysed



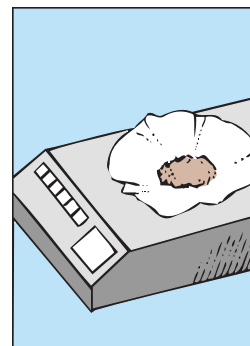
(b) Dissolving this sample in water



(c) Adding a suitable chemical to form a precipitate



(d) Filtering to collect the precipitate



(e) Repeated drying and weighing until a constant mass of precipitate is obtained

SAMPLE PROBLEM 12.3

The phosphate content of a detergent has been determined gravimetrically. The method used was the quantitative precipitation of the phosphate as magnesium ammonium phosphate-6-water, followed by collection and weighing of the precipitate. The procedure used is summarised below.

A solution of the detergent was made by dissolving 1.00 gram in 100 mL of warm water. Three millilitres of concentrated hydrochloric acid was added to the solution. A 25 mL solution of 10% (w/v) magnesium chloride and 20% (w/v) ammonium chloride was then added. Finally, concentrated ammonia was stirred into the mixture until the mixture was slightly alkaline. Crystals of magnesium ammonium phosphate-6-water formed slowly. The crystals were finally filtered and dried by washing with ethanol and then ether. The crystals were transferred to a desiccator for 30 minutes before weighing.

The equation for the precipitation reaction is:



- (a) Explain the purpose of:
- washing the precipitate with ethanol and ether
 - using a desiccator in the experiment.
- (b) The following results were collected on weighing the crystalline precipitate:
- mass of dry filter paper and Petri dish = 25.345 g
mass of filter paper and Petri dish + dried crystals = 25.665 g
- Calculate the mass of magnesium ammonium phosphate-6-water crystals collected.
 - Calculate the mass of phosphate present in this quantity of crystals.
 - Thus, determine the percentage by mass of phosphate in the detergent.
- (c) Identify experimental procedures that will affect the accuracy and reliability of the experiment.

SOLUTION

- (a) (i) The ethanol and the ether help to remove traces of water from the precipitate. Water is quite soluble in ethanol. Ethanol in turn is soluble to some extent in ether. Ether is also very volatile, and rapidly evaporates.
- (ii) The desiccator contains drying crystals that remove traces of free water from the precipitate prior to weighing.

The drying crystals are composed of anhydrous, blue silica gel, which turns pink when it absorbs water. In this case, a desiccator is used, rather than an oven, as the crystals are hydrated; too high a temperature could cause them to dehydrate and, therefore, change their composition.

- (b) (i) $m = \text{mass of crystals} = 25.665 - 25.345 \text{ g}$
 $= 0.320 \text{ g}$
- (ii) Molar weight (M) of magnesium ammonium phosphate-6-water = 245.418 g/mol
Percentage by weight of PO_4 in magnesium ammonium phosphate-6-water
 $= M(\text{PO}_4) / M \times 100 / 1 = 94.97 / 245.418 \times 100 / 1$
 $= 38.70\%$
Mass of phosphate in the crystals collected
 $= 38.70 / 100 \times 0.320$
 $= 0.124 \text{ g}$
- (iii) Percentage phosphate in detergent
 $= 0.124 / 1.00 \times 100 / 1$
 $= 12.4\% \text{ (w/w)}$

(c) Accuracy and reliability

The accuracy of a measurement is determined by how close the measurement is to the true or accepted value.

1. Use a greater mass of detergent so that the weight of the precipitate collected is greater. This reduces the percentage error in the experiment.
2. Ensure that a precision electronic balance is used (e.g. it should weigh to 3 or 4 decimal places). Ensure the electronic balance is calibrated.
3. Ensure that the filter papers are dried to constant mass prior to use. An alternative to filter paper is a sintered glass filter that can be dried accurately to constant weight.
4. Ensure that all the precipitate is quantitatively transferred and that the precipitate is dried to constant weight. This can be checked by repeated drying until no change in weight occurs.

For this experiment to be reliable, it is essential to show that repeated measurements achieve the same result within the limits of experimental design. Statistically, it is important to repeat measurements a minimum of five times to ensure reliability. It is important to control all variables and to perform each repeat experiment with the same levels of precision. When repeated experiments are within a narrow range (i.e. the standard deviation is small) then reliability has been achieved.

Students should check Appendix 1 on page 653 for more information on accuracy and reliability.

12.2 PRACTICAL ACTIVITIES

Sulfate content of a fertiliser



12.3 DATA ANALYSIS

Gravimetric analysis



SYLLABUS FOCUS

24. USING INSTRUCTION TERMS CORRECTLY

When answering questions it is important to know what the instruction terms ('verbs') require you to do. Here are some examples:

'Evaluate'

This instruction word requires you to make a judgement based on criteria or to determine the value of a process or concept.

Example:

Evaluate the use of gravimetric analysis in determining the chemical composition of materials such as lawn fertilisers.

Answer:

Gravimetric analysis is a quantitative technique used by chemists to determine the percentage by weight of a specific element or ion in a substance. The technique relies on extracting the specific element or ion from the substance and converting it into a new material that can be isolated, purified and weighed. Most gravimetric analyses rely on the production of precipitates from solutions of the substance being analysed.

In the case of lawn fertilisers, there may be both soluble and insoluble components. Thus, a chemist must find a means of dissolving the whole material. This is often done by digestion with a concentrated acid such as nitric acid, as nitrates are soluble. Lawn fertilisers commonly contain various ions including potassium, ammonium, sulfate and phosphate. The sulfate of phosphate content can be determined gravimetrically whereas the potassium and ammonium content cannot, as these ions do not form insoluble compounds. Volumetric analysis can be used to determine the ammonium levels in a lawn fertiliser, and an instrumental technique such as atomic

absorption spectrometry can be used to determine the potassium content.

Sulfate ions are commonly determined by precipitation of the insoluble barium sulfate. This procedure achieves high levels of precision as long as the fine particles of precipitate are coagulated to prevent them passing through the filter, and the precipitate is washed thoroughly to remove adhering ions. The barium sulfate and filter are weighed to constant dryness and the mass of barium sulfate determined. Phosphate can also be determined by quantitative precipitation as magnesium ammonium phosphate-6-water. This hydrated precipitate can be dried only in a desiccator, as too high a temperature will lead to dehydration.

The use of gravimetric techniques relies on following standard procedures to ensure that the final product to be weighed is pure and dry. Gravimetric procedures are subject to interference from other ions. For example, the precipitation of sulfate using barium ions must be performed in acidic solution to ensure that no carbonate ions are present. These carbonate ions would also precipitate with the barium ions.

Because gravimetric analysis is a 'wet' procedure (i.e. requiring a chemist to perform analyses using standard separation methods involving chemicals) it is much more time consuming than more modern instrumental methods, whereby the sample is injected into a machine that does the analysis.

If all the experimental requirements are met, then gravimetric methods are highly suitable for quantitative analysis of materials such as fertilisers.

12.1 Questions

1. Identify the coloured ions in the following list.



2. (a) Describe the procedure for conducting a flame test.
(b) A white salt gives a brick-red flame test. Identify a possible cation that may be present in this white salt.

- (c) Describe a confirmatory test based on a precipitation reaction.

3. Describe chemical tests that will distinguish between the following pairs of ions in solution.
(a) Calcium ions and barium ions
(b) Barium ions and lead (II) ions
(c) Copper (II) ions and iron (III) ions
4. Describe a chemical test that will distinguish between solid samples of the following compounds.

- (a) potassium chloride and potassium sulfate
 (b) iron (II) chloride and iron (III) chloride
 (c) calcium nitrate and lead (II) nitrate.
5. Drops of nitric acid are added to a white salt. Rapid effervescence occurs. State one conclusion that could be made from this test concerning the white salt.
6. A student, Bronia, tested a white solid using the following elimination sequence.
- A small amount of the white solid was placed in a tube and dilute nitric acid was added. The solid dissolved in the acid without effervescence.
 - Drops of barium nitrate solution were added to the colourless solution from step(i), but no further change was observed.
 - The acidic solution from step (ii) was then tested with drops of silver nitrate solution. Bronia noticed that a white precipitate formed.

Use Bronia's collected data to:

- determine which anions have been eliminated
 - identify the anion present in the white solid
 - describe a confirmatory test that could be used.
7. During a practical examination, Peter used the following information to identify two cations in a mixture.
- Peter was told that the two cations were from the following list:



The table below lists the sulfide salts that are soluble under acidic or alkaline conditions. All other sulfides are insoluble in acidic or basic conditions. Hydrogen sulfide gas is a useful source of sulfide ions when bubbled through aqueous solutions.

Sulfide salts soluble in acidic solution	Sulfide salts soluble in alkaline solution
Na ₂ S, K ₂ S, BaS, CaS, MgS, Al ₂ S ₃ , CoS, ZnS, FeS, (NH ₄) ₂ S	Na ₂ S, K ₂ S, BaS, CaS, MgS, (NH ₄) ₂ S

Peter tested the unknown solution as follows:

- The solution was acidified with dilute hydrochloric acid. No change was observed.

- Using a fume cupboard, Peter passed hydrogen sulfide (H₂S) gas into the acidic solution; a black precipitate formed. The gas was allowed to pass through the solution until no further precipitation occurred. The mixture was filtered and the filtrate used in the next test.
- The filtrate was made slightly alkaline (pH~9) and then hydrogen sulfide gas was passed through the mixture. A black precipitate formed.

Use this information to identify the two cations in Peter's mixture. Justify your response.

8. Copy and complete the following table by writing the chemical formula of any precipitate that may form when the reagent is added to the cation solution. Where no precipitate forms write 'no reaction'.

Cation	Sodium chloride	Sodium sulfate	Sodium hydroxide	Sodium carbonate
Pb ²⁺				
Cu ²⁺				
Ca ²⁺				

9. Answer this question when you have completed Practical activity 12.2. Explain the importance of the following procedures in the determination of the sulfate content of a lawn fertiliser.
- Acidifying the solution after dissolving the weighed fertiliser in water
 - Adding an excess of a solution of barium ions
 - Boiling the suspension of barium sulfate
 - Washing the barium sulfate precipitate on the filter paper
 - Weighing to constant dryness
10. A sample of 3.150 g of a soluble lawn fertiliser was analysed for its sulfate content by gravimetric analysis. The sulfate was weighed as barium sulfate. The mass of barium sulfate collected was 3.325 g.
- Identify whether gravimetric analysis is a qualitative or quantitative procedure.
 - Write an ionic equation for the precipitation reaction used in this experiment.
 - Calculate the percentage by weight of barium sulfate in the fertiliser.

12.2 INSTRUMENTAL ANALYSIS

Remember

Before beginning this section, you should be able to:

- identify the need for collaboration between chemists as they collect and analyse data
- extract information from numerical data in graphs and tables.

Key content

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

- describe the use of atomic absorption spectroscopy (AAS) in detecting concentrations of metal ions in solutions and assess its impact on scientific understanding of the effects of trace elements
- gather, process and present information to interpret secondary data from AAS measurements, and evaluate the effectiveness of this in pollution control
- gather, process and present information to describe and explain evidence for the need to monitor levels of one of the above ions in substances used in society.

Atomic absorption spectroscopy (AAS)

When you look at a blue copper sulfate solution in a beaker, your eyes are detecting visible wavelengths that have been transmitted from the solution. Some of the wavelengths of the white light passing into the solution have been absorbed, whilst the others have been transmitted. Atomic vapours also selectively absorb and emit various frequencies of light. If a sample of an element is vapourised in a hot flame, electrons are promoted from the ground state into unstable or excited energy levels. As the electrons fall back to more stable levels they emit light of characteristic frequencies and wavelength. If white light is passed through an atomic vapour at a suitably low temperature to prevent electron excitation, some wavelengths are selectively absorbed and dark lines appear in the spectrum produced (Figure 12.8).

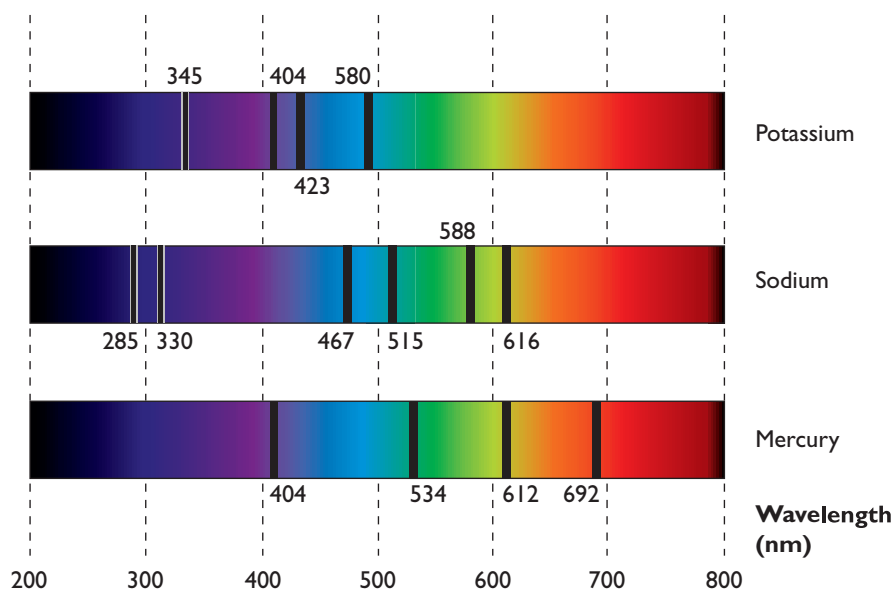


Figure 12.8 The lines in the atomic absorption spectrum are a 'fingerprint' for each element.

spectrometer: device that detects and measures a substance by its absorbance of certain wavelengths of light from the electromagnetic spectrum; also called spectrophotometer

These dark lines correspond to the exact bright line wavelengths in atomic emission spectra. The atomic absorption **spectrometer** (AAS) was



Figure 12.9

Alan Walsh is an Australian chemist who invented the atomic absorption spectrometer while working for CSIRO.

developed by Alan Walsh (a CSIRO scientist) using the principle of selective light absorption by metal ions. He realised that such a device could accurately measure the concentration of elements in minute amounts. This technique is very sensitive. It can detect concentrations in parts per million and sometimes in parts per billion.

the Researchers

Absorbing Atom

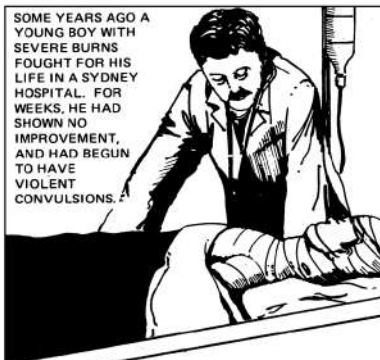
COMPLEX CHEMICAL ANALYSES WHICH ONCE TOOK DAYS CAN NOW BE PERFORMED IN MINUTES, WITH GREAT ACCURACY, ON SOLIDS AND LIQUIDS. SIXTY-SEVEN OF THE 92 NATURALLY-OCCURRING ELEMENTS CAN BE DETECTED.



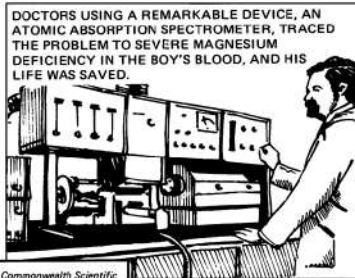
IN THE FOOD INDUSTRY, IT DETECTS CORROSION IN CANNED FOODS, MERCURY CONTENT IN FISH, AND COPPER, LEAD AND IRON LEVELS IN WINE.



SOME YEARS AGO A YOUNG BOY WITH SEVERE BURNS FOUGHT FOR HIS LIFE IN A SYDNEY HOSPITAL. FOR WEEKS, HE HAD SHOWN NO IMPROVEMENT, AND HAD BEGUN TO HAVE VIOLENT CONVULSIONS.

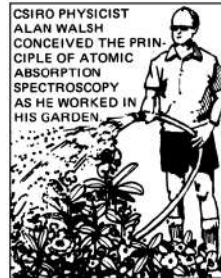


DOCTORS USING A REMARKABLE DEVICE, AN ATOMIC ABSORPTION SPECTROMETER, TRACED THE PROBLEM TO SEVERE MAGNESIUM DEFICIENCY IN THE BOY'S BLOOD, AND HIS LIFE WAS SAVED.

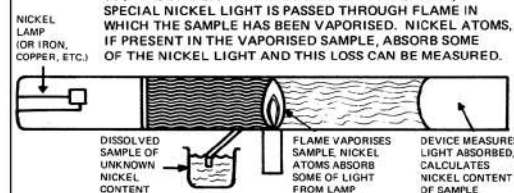


Commonwealth Scientific and Industrial Research Organization 4/76
Art: B. Gosnell
Script: G. O'Neill

CSIRO PHYSICIST ALAN WALSH CONCEIVED THE PRINCIPLE OF ATOMIC ABSORPTION SPECTROSCOPY AS HE WORKED IN HIS GARDEN.



THE BASIC PRINCIPLE OF ATOMIC ABSORPTION SPECTROSCOPY IS SIMPLE. IF THE ANALYSIS IS FOR NICKEL, A SPECIAL NICKEL LIGHT IS PASSED THROUGH FLAME IN WHICH THE SAMPLE HAS BEEN VAPORISED. NICKEL ATOMS, IF PRESENT IN THE VAPORISED SAMPLE, ABSORB SOME OF THE NICKEL LIGHT AND THIS LOSS CAN BE MEASURED.



OTHER METALS IN THE SAMPLE CAN BE MEASURED BY USING OTHER 'METAL' LAMPS. DR WALSH'S DEVICE HAS HAD A DRAMATIC EFFECT ON MINERAL EXPLORATION, SPEEDING UP ASSAYING OF ORE SAMPLES.



IN AGRICULTURE, ATOMIC ABSORPTION SPECTROSCOPY HAS HELPED SCIENTISTS STUDYING SOIL COMPOSITION, AND THE ROLE PLAYED BY METALLIC ELEMENTS IN LIVING TISSUE.



STEELMAKERS USE IT TO CHECK CRITICAL MAGNESIUM LEVELS IN STEEL WHILE ENGINEERS CAN ANALYSE OIL FROM DIESEL ENGINES TO MEASURE WEAR.



NOW MADE IN AUSTRALIA, THE US, JAPAN AND BRITAIN, THE ATOMIC ABSORPTION SPECTROMETER IS USED IN MANY COUNTRIES, AND HAS EARNED MILLIONS OF EXPORT DOLLARS FOR AUSTRALIA.



Figure 12.10

The development of AAS has allowed chemists all over the world to analyse very small amounts of metals in various materials.

Figure 12.11 shows how this atomic absorption spectrometer (AAS) spectrometer works.

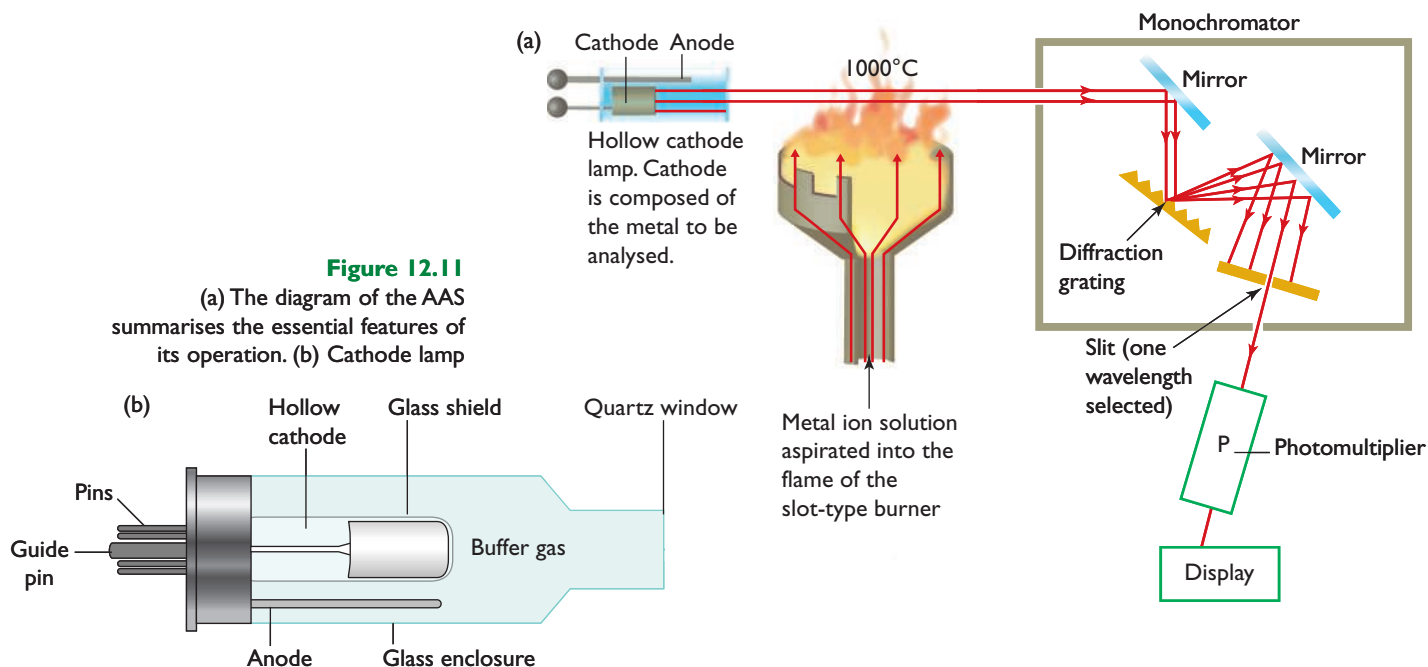


Figure 12.11

(a) The diagram of the AAS summarises the essential features of its operation. (b) Cathode lamp

(b) Hollow cathode, Glass shield, Quartz window, Pins, Guide pin, Anode, Glass enclosure, Buffer gas

Hollow-cathode lamp selection

The light source in the atomic absorption spectrometer is usually a hollow-cathode lamp of the element that is being measured. So, if the concentration of lead in a water sample is to be determined, the AAS lamp uses a lead cathode. Specific wavelengths of light characteristic of the element being analysed are generated from this lamp.

Standard solution preparation

A standard solution of the metal to be analysed is prepared using standard volumetric techniques. This solution is then diluted systematically to obtain diluted standard solutions.

Aspirating the solutions

The dilution standards and the unknown solution are sprayed or aspirated in turn (using a nebuliser) into the flame. Alternatively, the sample can be heated in a graphite furnace. A flame AAS uses a slot type burner (~1000°C) to increase the total absorbance of light. The graphite furnace (~3000°C) is more efficient than the flame method in that it can be used for smaller quantities of material, as well as providing a reducing environment for samples that are readily oxidised.

Measuring light absorption

monochromatic: light of a single (or very narrow) wavelength

As the light beam passes through the vapourised sample, some of the light is absorbed by the hot atoms. A second reference beam bypasses the sample. The emerging light beams pass through a monochromator which contains a diffraction grating and focussing mirrors. The light then passes through a narrow slit to select only one of the wavelength bands to be measured. The light is now said to be **monochromatic**. For example, a wavelength of 422.7nm is used to determine the concentration of calcium in a hard-water sample. The intensity of this selected beam is then measured.

Photomultiplier tubes are the most common detectors for AAS. They measure the light intensity and convert it into an electrical signal.

The amount of light absorbed relative to the reference beam (measured by the absorbance, A) is related to the concentration, c , of element in the vapourised sample. The greater the concentration the greater the amount of light absorbed.

$$A = kc$$

The constant k depends on the characteristic of the apparatus and the metal being analysed.

Calibration

calibration: correlating readings with a standard or series of standards

Concentration measurements are usually determined from a **calibration** curve created with the standards of known concentration. A control blank that contains only the solvent is also run. This blank should register zero absorbance.

Table 12.6 lists some of the main absorption lines in the visible spectrum for a variety of metals.

Table 12.6 Main absorption line wavelengths in the visible spectrum (nm)

Metal	Absorption line wavelengths (nm)
barium	649, 614, 578, 554, 493
cadmium	644, 510
mercury	578, 546, 492, 436
potassium	580, 423, 404
sodium	616, 588, 515, 467

SAMPLE PROBLEM 12.4

The calcium ion concentration for two samples of water (X and Y) were determined using AAS. The absorbance of some standard solutions was first measured at a wavelength of 422.7 nm. The results are tabulated.

[Ca ²⁺] (ppm)	1	5	10	25	50
Absorbance (A)	0.0065	0.0275	0.0555	0.1395	0.2790

The two samples of water were measured and their absorbances were:

$$A_X = 0.2500$$

$$A_Y = 0.1500$$

Use this information to:

- construct a calibration graph
- determine the calcium ion concentration in the water samples.

SOLUTION

- Calibration graph

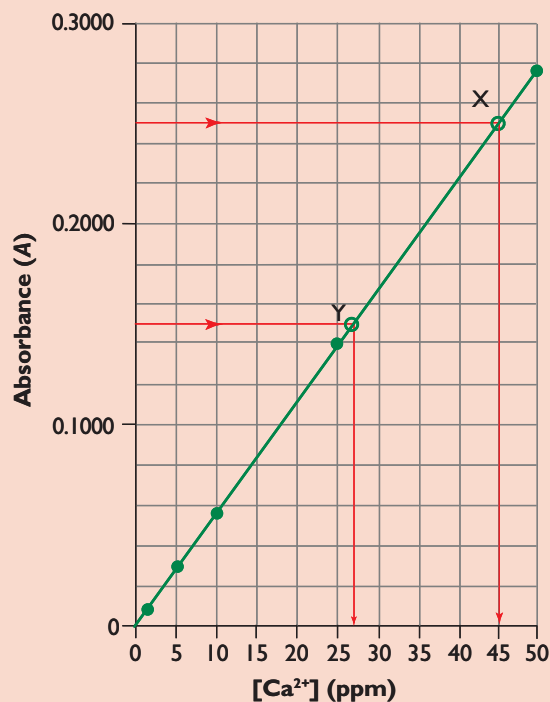


Figure 12.12 The calibration graph relates the absorbance to the calcium ion concentration.

- Interpolate calcium ion concentration from the graph.

$$c_X = 45 \text{ ppm}$$

$$c_Y = 27 \text{ ppm}$$

Monitoring trace elements and pollutants in the environment

Atomic absorption spectroscopy is a useful tool in measuring the concentration of trace metals and heavy metals in the environment.

Essential trace elements

essential trace element: elements that are required by living organisms in very small (trace) quantities (typically 1–100 ppm)

There are many metallic and non-metallic elements that are needed in small quantities by plants and animals for the proper functioning of their physiological processes. These **essential trace elements** include copper, zinc, cobalt and molybdenum.

These trace elements are obtained by human beings and animals through the food they eat. Plants absorb various minerals from the soil; when animals and humans eat these plants they absorb the essential micronutrients. If a soil is lacking in certain elements, humans or animals may exhibit deficiency diseases.

Table 12.7 lists the trace elements and ultra-trace elements essential for animal life.

Table 12.7 Trace elements essential for animals

Classification	Examples
Metal	V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, W, Sn
Semi-metal	Si, Se
Non-metal	F, I

The existence of these trace elements was not known until sensitive analytical methods such as AAS were developed. The old ‘wet’ methods involving gravimetric or volumetric analysis were too insensitive to detect low levels of metal ions. They were also very time consuming. AAS is very specific as it can determine the concentration of a metal ion in the presence of other metals. The other metal ions do not usually interfere with the absorbance measurements because the specific wavelength used is absorbed only by the metal being analysed. ‘Wet’ methods often failed when other ions were present, as they may also react with the added reagents. Some anions may interfere during AAS where thermally stable compounds are formed. However, techniques have been developed to overcome this problem.

Using AAS, scientists can quickly and reliably establish which trace metals are required for specific biochemical pathways. This has had a large impact on our understanding of the functioning of the body. Prior to these developments, deficiency diseases could not be explained. By using AAS as an analytical tool, chemists have discovered that trace elements have a variety of essential roles. These include:

- copper — required for the production of enzymes involved in biochemical oxidation reactions; acts as a catalyst in the formation of haemoglobin
- iron — required for the production and functioning of haemoglobin in the blood
- cobalt — a component of vitamin B12; vital for the production of haemoglobin
- chromium — required for carbohydrate, fat and nucleic acid metabolism; component of the glucose tolerance factor required for insulin action
- zinc — needed for amino acid metabolism and energy production; associated with enzymes that produce insulin; associated with the

development of immune (T and B) cells; involved in the regulation of bone calcification

- manganese — required for blood clotting as well as fat and carbohydrate metabolism
- iodine — required for the proper functioning of the thyroid gland.

Deficiencies of these trace elements in the soil or in animal diets leads to significant health problems. Blood and urine samples in humans or sap samples in plants can be analysed by AAS, and an analytical chemist can quickly determine whether the concentration of a trace element is within normal limits. Using AAS, chemists can also assist sheep farmers in determining whether their soils are deficient in molybdenum, zinc, manganese and copper. If these trace metal levels are low then sheep that are feeding on trace metal deficient grass will not be healthy. Trace elements can then be included in fertilisers to ensure the soil is fertile.

Heavy metal pollutants

Heavy metals include elements such as lead, mercury, cadmium and chromium. Heavy metal ions are toxic to humans and animals.

Mercury and other heavy metal pollution in waterways and the soil is of great concern. When mercury is present in water, it is absorbed by various organisms, and becomes concentrated in their flesh. Some bacteria convert the inorganic mercury ions to organic mercury compounds. Oysters and other filter feeders filter polluted water, and their tissues can readily become contaminated with organic mercury and other heavy metals such as lead and cadmium. Other organisms that feed off these contaminated oysters and mussels concentrate the mercury in their own bodies. The EPA requires that industrial wastewater should not be released into waterways unless it is first diluted to produce mercury levels less than 2 ppm. Human food, such as fish and other seafood, should contain no more than 0.5 ppm of mercury.

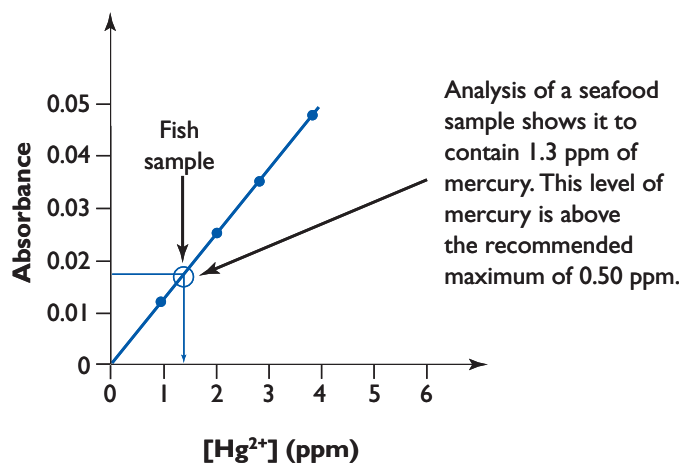
AAS can be used to measure the mercury levels in seafood. The first step involves the freeze-drying of the tissue. A sample is then weighed and the mercury extracted using concentrated nitric acid. The mixture is filtered and the filtrate is diluted systematically in a volumetric flask. A series of mercury standards is also prepared. These standard solutions are vapourised in the AAS and a calibration graph established. The unknown seafood solution is then measured and the mercury concentration determined from the calibration graph.

The tragedy of Minamata disease in the 1950s exposed the dangers of heavy metal poisoning. The people of this fishing village in Japan became ill and many died due to the eating of fish contaminated with mercury from an industrial complex.

The mercury entered the food chain through the activity of bacteria that converted inorganic mercury into organic mercury.

Figure 12.13
The concentration of mercury in seafood can be determined using AAS.

12.4 DATA ANALYSIS
Monitoring lead pollution and using AAS in pollution control



SYLLABUS FOCUS

25. 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:

'Assess'

This instruction word requires you to make a judgement of value, quality, outcome, results or size. A balanced judgement is important in your response.

Example:

Assess the impact of AAS on the scientific understanding of the effects of trace elements.

Answer:

Trace elements are elements that are required by all living organisms in very small (trace) quantities. In high doses, trace elements can be toxic.

The development of sensitive analytical methods such as AAS allowed chemists to detect metal ions in very low (e.g. ppm or ppb) concentrations. This led to the discovery that living things required some ions at very low levels to maintain their biochemical functions. The old analytical techniques that relied on 'wet' methods (e.g. gravimetric or volumetric analysis) were too insensitive to detect such low levels of ions.

AAS allows chemists to conduct analyses very rapidly and in multiple batches. This was not possible with older 'wet' methods that were very time consuming. Reliability of results was therefore improved as many repetitions of the measurement could be quickly made.

AAS allowed chemists to investigate the role of trace elements in a wide variety of situations. These include:

- conducting soil analyses to assist farmers to monitor and manage the levels of essential trace elements; soils that are poor in trace elements will not produce good crops or provide grazing animals the mineral requirements for strong, healthy growth
- blood and urine analysis to detect anomalies in metabolism due to an trace metal deficiencies; these deficiencies can then be prevented by appropriate changes to the diet
- analysis of trace metals in hair using AAS, which has established a link between trace mineral levels and behavioural disorders, cardiovascular disease, and some cancers
- research that has revealed the importance of the trace metal lithium in stabilising mood swings in people.

These examples demonstrate that the development of instrumental techniques such as AAS have had major health benefits for communities, as well as benefits to agriculture and therefore the economy of our nation.

12.2 Questions

1. Answer the following questions in relation to the flame atomic absorption spectrometer.
 - (a) Identify the source of the light in AAS.
 - (b) Explain what happens to the light from the lamp as it passes through the flame of the burner.
 - (c) Explain why the light passing into the detector is classified as monochromatic.
 - (d) Describe the relationship between absorbance and concentration of metal ions in the sample.
 - (e) Explain why a solvent blank is also run through the apparatus.
2.
 - (a) Define the term *trace element*.
 - (b) Identify three trace metals important to the health of humans and describe the reason for their importance.
 - (c) Explain how an analytical chemist could determine whether the level of a specific trace metal in blood was within the normal range for good health.
3. Soils in some locations are poor in certain trace metals such as molybdenum, zinc and manganese.
 - (a) Identify the problems associated with depleted trace metal levels in such soils.
 - (b) Describe how such problems can be monitored and corrected.

4. Figure 12.14 shows a calibration graph used to determine the concentration of trace quantities of lead (II) ions in a sample of polluted water.
- Identify an instrumental method that could be used to measure the absorbance of each standard lead (II) ion solution.
 - Use the calibration graph to determine the concentration of lead (II) ions in a water sample that gives an absorbance reading of 0.8. Express your answer in parts per million.

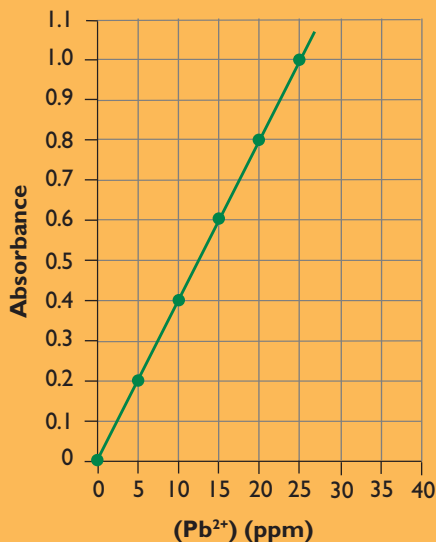


Figure 12.14 Use this calibration graph to answer question 4.

- Describe problems associated with high levels of lead in the environment.
 - Describe how AAS can assist in monitoring lead levels in the environment.
- An analytical chemist collected river water samples to investigate the concentration of mercury ions in three different locations (A, B and C). Back in the laboratory he analysed these solutions using AAS. He prepared his dilution standards and measured their absorbance. The seawater samples were first diluted systematically by a factor of 1 in 5. He then measured the absorbance of his three diluted unknown samples.

The results are tabulated below.

Standards:

Standard	1	2	3	4	5
[Hg ²⁺] (ppm)	1	2	4	6	10
Absorbance (A)	0.013	0.025	0.051	0.075	0.120

Diluted unknowns:

Unknowns	A	B	C
Absorbance (A)	0.020	0.040	0.065

- Draw a calibration graph and construct a line of best fit through the data points.
 - Use the calibration graph to calculate the mercury ion concentration in each water sample.
 - Mercury ion concentrations in rivers and streams of 2 ppm or greater are a concern for public health. In potable water the level should be below 0.001 ppm. Identify the samples that have mercury levels that are of concern.
7. An old industrial site in which mercury thermometers were manufactured was investigated for mercury pollution of the soil. A sample of soil was collected from one location at the site and returned to the laboratory for analysis. A trainee chemist took the sample and digested it in hot nitric acid to extract the mercury ions. The sample was then filtered and the filtrate diluted in a beaker until its volume was 100 mL. The absorbance of this solution was measured using an atomic absorption spectrophotometer. Normal tap water was also measured.

Deionised water was used as a blank.

- Explain the additional solutions that need to be prepared, and the measurements that need to be performed, by the chemist to determine the mercury levels in the soil sample.
 - Discuss problems with the methods used by the trainee chemist, and explain how they can be improved.
 - The absorbance of the sample was not very different from normal tap water samples. The chemist concluded that the soil at the site was not contaminated with mercury. Assess the validity of this conclusion and explain how more-reliable data could be obtained.
8. A student, Joel, is asked to prepare a stock solution of magnesium chloride and then to prepare a series of dilution standards from the stock that could be used to construct a calibration graph for AAS measurements. The stock solution is to have a concentration of 1000 ppm Mg²⁺ (1000 mg/L). The dilution standards are to have concentrations of 10, 8, 6, 4, 2 and 1 ppm Mg²⁺.
- Joel is provided with a sample of pure magnesium ribbon.
- Describe the procedure that Joel will adopt to prepare these solutions.

9. Figure 12.17 is a simplified drawing of a flame atomic absorption spectrometer. The parts are labelled with code letters. Draw up a table to identify the components and state the function of each.

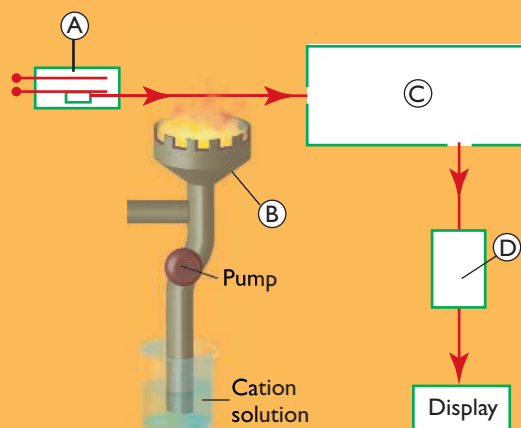


Figure 12.17

10. Figure 12.15 shows the AAS calibration graph for standard solutions of cadmium ions.

Figure 12.16 is a map of a river catchment. The map shows the location of various types of industry. All these industries discharge effluents into the river catchment.

An analytical chemist collected water samples at five different locations (A, B, C, D and E) as shown on the map. She analysed these samples for cadmium ion concentration using AAS. The absorbances of the five samples are tabulated below.

Sample site	A	B	C	D	E
Absorbance (A)	0.06	0.07	0.12	0.70	0.45

- Explain the chemist's choice of lamp for use in the spectrometer.
- Justify your conclusion about the likely source of cadmium pollution.
- Calculate the cadmium ion concentration at the most polluted site.

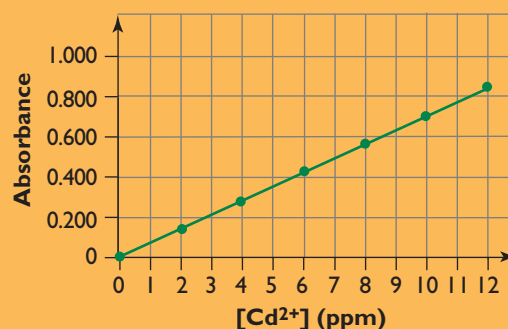
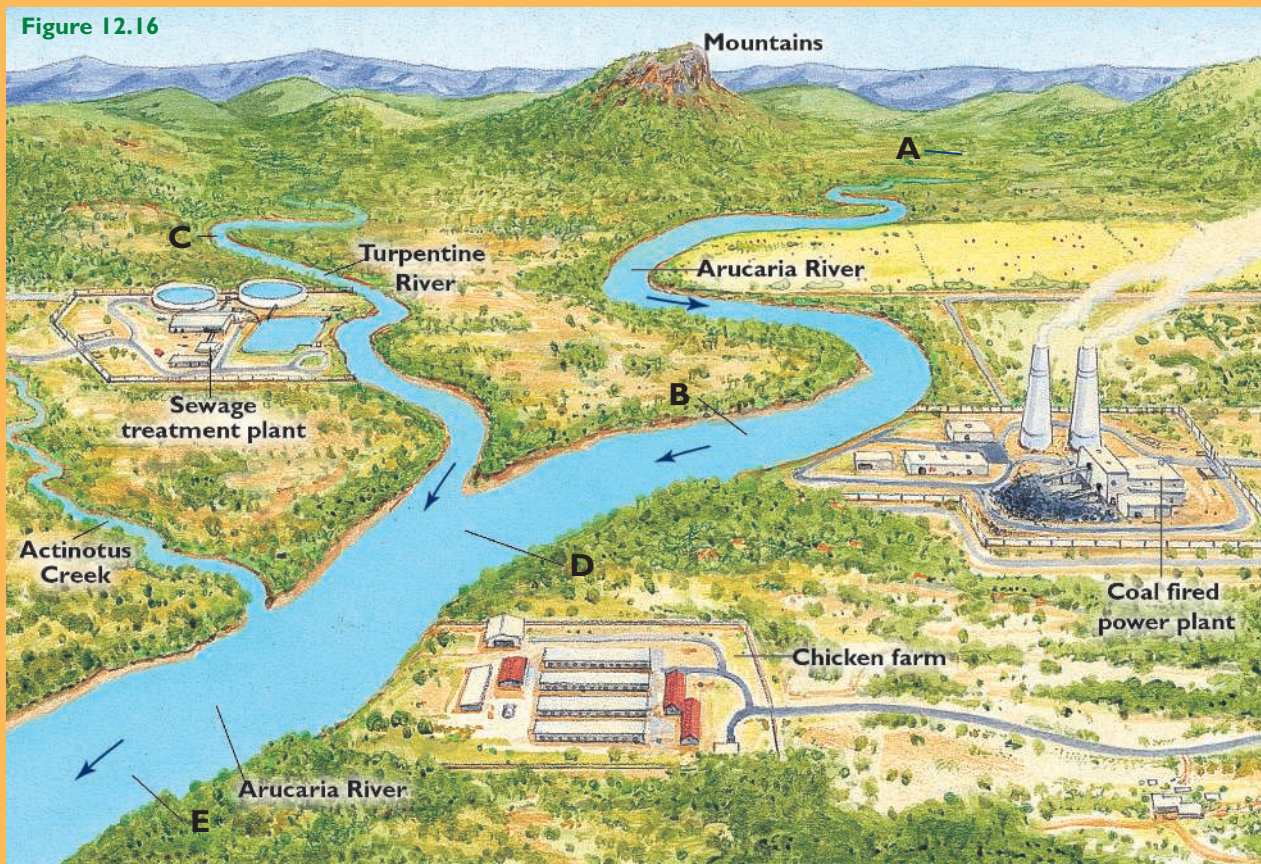


Figure 12.15

Figure 12.16





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CHECKPOINT REVISION 3

SUMMARY

- Analytical chemists can identify and monitor the concentrations of various ions in aqueous systems.
- Mixtures of ions can be identified using a variety of qualitative chemical tests.
- The amount of a specific ion in a solution or other material can be determined by quantitative techniques such as gravimetric analysis.
- The sulfate content of a soluble lawn fertiliser can be determined by precipitating the sulfate as insoluble barium sulfate and weighing the dried precipitate.
- Modern analysis of metals involves the use of instruments such as atomic absorption spectrometers.
- AAS is a technique in which a solution of a metal ion is sprayed into a flame and the amount of light of a specific wavelength that is absorbed by the vapourised metal ions is used to determine the concentration of the metal.
- Atomic absorption spectroscopy can measure trace quantities of metals in materials. This has allowed chemists to identify trace metals in our bodies and in the foods we eat as well as determine the degree of pollution by heavy metals.
- Essential trace elements are those elements that are required by living organisms in very small (trace) amounts.

PRACTICAL ACTIVITIES

12.1 PRACTICAL ACTIVITIES

IDENTIFICATION OF IONS

Aim

To perform a range of chemical tests to identify common cations and anions

Safety

- Wear safety glasses throughout this experiment.
- Concentrated HCl used for flame tests is dangerous.
- Identify other safety precautions relevant to this experiment by reading the method.

Materials

- test tubes
- platinum or nichrome wire in glass holder
- dropper bottles containing the following solutions:

Anion tests

- 0.1 molar solutions of sodium carbonate, sodium chloride, sodium sulfate, sodium phosphate, silver nitrate
- 1 molar solutions of nitric acid, barium chloride, barium nitrate

Flame tests

- solid samples and atomiser bottles containing solutions of: potassium chloride, iron (III) chloride, calcium chloride, barium chloride, copper (II) chloride
- concentrated HCl

Cation tests

- 0.1 molar solutions of lead (II) nitrate, potassium iodide, copper (II) nitrate, calcium nitrate, barium nitrate, iron (III) nitrate
- 1 molar solutions of sodium chloride, sodium sulfate, sodium hydroxide, sodium carbonate

Other reagents

- 1 molar ammonia solution, 4 molar ammonia solution, dilute potassium hexacyanoferrate (III) ($K_3Fe(CN)_6$), dilute potassium thiocyanate reagent (KSCN)
- solids: iron (II) ammonium sulfate
- distilled water

Part A: Anion tests

Method

These tests are best conducted in semi-micro or small test tubes.

Place 20 drops of the solution to be tested in a test tube. Follow the procedure for each test. Copy the following table into your book, and record your observations.

Anion	Procedure	Observation
CO_3^{2-}	To 20 drops of 0.1 molar sodium carbonate solution add up to 20 drops of 1 molar nitric acid, and warm in a hot-water bath. Repeat the test with tap water as a control.	
CO_3^{2-}	To 20 drops of sodium carbonate solution add 2–10 drops of 1 molar barium nitrate (or chloride) solution.	
CO_3^{2-}	To 20 drops of sodium carbonate solution add 2–10 drops of 0.1 molar silver nitrate solution.	
SO_4^{2-}	To 20 drops of 0.1 molar sodium sulfate solution add 2–5 drops of 1 molar barium nitrate (or barium chloride solution).	
SO_4^{2-}	To 20 drops of 0.1 molar sodium sulfate solution add 2–5 drops of 0.1 molar silver nitrate solution.	
Cl^-	1. To 20 drops of 0.1 molar sodium chloride solution add 3 drops of 0.1 molar silver nitrate. 2. Check that the precipitate formed dissolves in 4 molar ammonia solution. Repeat the silver nitrate test with a distilled water control.	
PO_4^{3-}	To 20 drops of 0.1 molar sodium phosphate solution* add 5–10 drops of 0.1 molar silver nitrate.	
PO_4^{3-}	To 20 drops of 0.1 molar sodium phosphate solution* add 5–10 drops of 1 molar barium nitrate (or barium chloride) solution.	

(* The sodium phosphate solution is mildly alkaline; if phosphate ions are present in acidic solution, ammonia should be added to raise the pH to about 10.)

PRACTICAL ACTIVITIES

Questions

Use your results to answer these questions.

- (a) Explain the appearance of gas bubbles in the test for carbonate ions. Write a balanced equation to account for these observations.
(b) State a confirmatory test which proves that the gas evolved is carbon dioxide.
- Explain why the silver nitrate test for chloride ions must be done in an acidified solution.
- Explain how a solution of potassium phosphate can be distinguished chemically from a potassium sulfate solution.
- A solution contains Cl^- , CO_3^{2-} , SO_4^{2-} and PO_4^{3-} ions.
(a) Identify a reagent that can be added to a sample of this solution that will identify only one of these anions.
(b) Barium nitrate solution is added in excess to a sample of the solution. Precipitation is observed. The mixture is then filtered. Identify which of the original four anions is present in the filtrate. Suggest a confirmatory test for this anion.

Part B: Flame tests for cations

- Solutions of various salts (preferably chloride salts) are provided in atomiser bottles.
- Place old newspaper on the bench. Place a lit Bunsen burner on the paper. Carefully spray the salt solution through a blue Bunsen burner flame and note the colour produced. Note that some salts may produce a yellow colour in the flame due to contamination with sodium ions. Copy the following table and record your observations.

Ion	Flame colour
K^+	
Fe^{3+}	
Ca^{2+}	
Ba^{2+}	
Cu^{2+}	

- These tests can also be repeated using a platinum or nichrome wire supported in a glass holder. The wire is dipped and cleaned in concentrated HCl until it produces no flame colour. The wire is then dipped in HCl and then in some powdered salt containing a particular cation (e.g. BaCl_2 , CaCl_2) and held in the edge of the upper blue zone of the Bunsen flame. The same colours are observed as with the atomiser test.

Questions

- Explain how flame tests could be used to distinguish between the following solutions.
(a) calcium chloride and barium chloride
(b) copper (II) chloride and barium chloride.
- Explain why flame tests would not be used to identify iron (III) ions.

Part C: Cation tests

These tests are best conducted in semi-micro or small test tubes.

Place 20 drops of the cation solution to be tested in a test tube. Add drops of the selected reagent until no further change is seen. Copy the following table and record your observations.

Cation	Reagent			
	Sodium chloride	Sodium sulfate	Sodium hydroxide	Sodium carbonate
Pb^{2+}				
Ca^{2+}				
Ba^{2+}				
Cu^{2+}				
Fe^{3+}				

Additional cation confirmation tests

The observations you have made in the previous tests indicate the presence or absence of various cations. Chemists do confirmatory tests to improve the reliability of experiments.

Method

Place 20 drops of the cation solution in a test tube and follow the procedure. Copy the following table and record your observations.

PRACTICAL ACTIVITIES

Cation	Procedure	Observation
Pb ²⁺	To 20 drops of 0.1 molar lead (II) nitrate, add 2–3 drops of 0.1 molar potassium iodide solution.	
Cu ²⁺	To 20 drops of the 0.1 molar copper (II) nitrate solution add drops of 4 molar ammonia solution . Continue to add ammonia (with stirring) until no further change occurs.	
Fe ²⁺	Dissolve a few crystals of iron (II) ammonium sulfate (a source of Fe ²⁺) in about 2 mL of 1 molar sulfuric acid. Add 5–10 drops of the yellow reagent potassium hexacyanoferrate (III) (K ₃ Fe(CN) ₆).	
Fe ³⁺	To 20 drops of iron (III) nitrate solution add drops of potassium thiocyanate reagent (KSCN).	

Questions

- Identify the cations that produce insoluble:
 - chlorides
 - sulfates
 - hydroxides
 - carbonates.
- Explain how samples of the following solutions can be distinguished.
 - barium chloride and calcium chloride
 - iron (II) sulfate and iron (III) sulfate
 - lead (II) nitrate and calcium nitrate
- Write ionic equations for the precipitation reactions observed for lead ions.
- Use the results of your experiment to design an elimination test for the five cations in a mixture.

Results and conclusion

Briefly describe the outcome of your investigation.

PRACTICAL ACTIVITIES

12.2

PRACTICAL ACTIVITIES



SULFATE CONTENT OF A FERTILISER

Aim

To use gravimetric analysis to determine the sulfate content of a lawn fertiliser (a mixed fertiliser containing ammonium sulfate and potassium (or ammonium) nitrate)

Safety

- Wear safety glasses throughout this experiment.
- Barium chloride solution is toxic.
- Identify other safety precautions relevant to this experiment by reading the method.

Background

The sulfate ion in the fertiliser is precipitated with barium ions from acid solution. The precipitate is collected, dried and weighed.

Materials

- solid (soluble) fertiliser (mixture of ammonium sulfate crystals with some potassium nitrate or ammonium nitrate)
- concentrated hydrochloric acid (dropper bottle)
- barium chloride solution — 7% (w/v)
- electronic balance
- 250 mL beaker
- burette
- hotplate
- glass rod
- watch glass
- quantitative filter paper

Method

Perform in teams and average the results of all teams.

1. Weigh out *accurately* approximately 0.60 g of the powdered lawn fertiliser into a clean 250 mL beaker. Record the mass of fertiliser.

Add 25 mL of warm water from a measuring cylinder. Stir to dissolve the crystals.

2. Add 10 drops of concentrated hydrochloric acid to the solution. (*Take care. Use safety glasses.*)
3. Use a hotplate to heat the mixture until it *just* boils.
4. Add from a burette the 7% barium chloride solution slowly to the hot sulfate solution until no further white precipitate forms. Stir with a glass rod after each addition. (You will need to allow the precipitate to *settle* and then add further drops of barium chloride to check that *all* the sulfate has precipitated.)
5. Gently re-boil the mixture for a further 5 minutes to coagulate the precipitate. Let stand on a fibreboard for 5–10 minutes to cool.
6. Meanwhile, weigh a circle of quantitative filter paper on an electric balance. Weigh a clock glass and record this weight.
7. Fold the filter paper into a cone and set up the apparatus for filtration.
8. Pour the warm supernatant and then the suspension of barium sulfate through the filter paper. Ensure that *all* the solid is transferred from the beaker to the filter using small amounts of *warm* washing water.
9. When filtration is complete, carefully transfer the opened filter paper to the weighed clock glass and allow to dry in a low temperature oven. Leave until the next lesson.
10. When they are dry, weigh the clock glass and filter. Calculate the mass of barium sulfate collected.

Results and conclusion

1. Calculate the number of moles of barium sulfate collected. Thus determine the number of moles of sulfate present in the fertiliser sample.
2. Calculate the weight of sulfate in the sample.
3. Calculate the percentage by weight of sulfate in the fertiliser.
4. Briefly describe the outcome of your investigation.

PRACTICAL ACTIVITIES

Questions

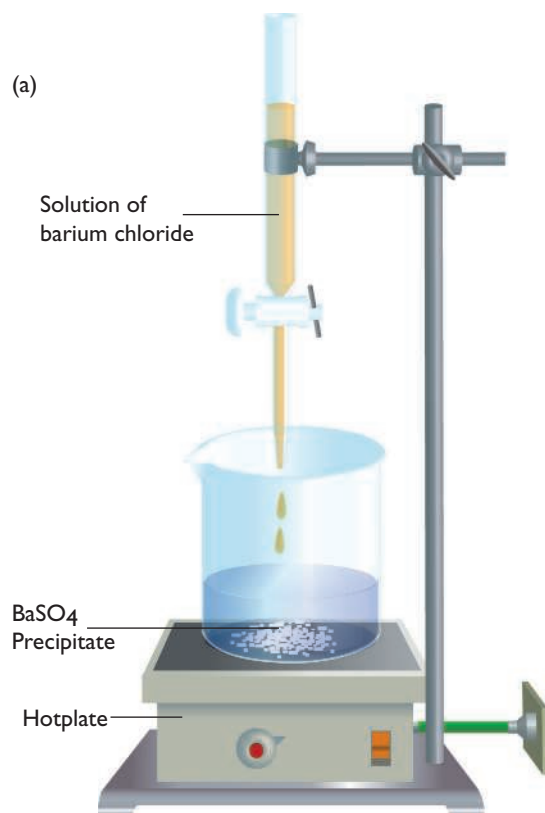
Answer the following questions in your report on this experiment.

1. Write a balanced ionic equation for the precipitation reaction.
2. Calculate the percentage by weight of sulfate ions in the fertiliser. Average the results of all groups and write the class average.
3. The solution is acidified prior to the addition of barium ions. Explain why the solution is acidified.
4. Explain why the precipitate is heated for some time prior to filtration.
5. One student considered varying the mass of fertiliser used in the experiment. Explain why the accuracy would be improved by precipitating 0.90 g of barium sulfate rather than 0.40 g of barium sulfate.
6. Explain why a quantitative filter paper leads to greater accuracy than using a qualitative filter paper.
7. Explain how reliability can be improved in this experiment.
8. On what assumption is the validity of the experiment dependent?
9. Explain why the precipitate on the filter paper should be heated to constant dryness.
10. The accuracy of the experiment can be improved by filtering through a pre-weighed fine-pore sintered glass filter rather than a filter paper. Explain why this procedure is more accurate.
11. Identify the main safety concerns in this experiment.

DATA ANALYSIS

12.3 DATA ANALYSIS GRAVIMETRIC ANALYSIS

A student was asked to gravimetrically determine the sulfate content of a lawn fertiliser. She weighed out 0.200 g of fertiliser and transferred it quantitatively to a 500 mL beaker using a little distilled water. Following acidification with a few drops of concentrated hydrochloric acid, the mixture was gently heated to boiling on a hotplate. A 5% (w/v) barium chloride solution was set up in a burette above the beaker and barium chloride solution added slowly until no further white precipitate formed. Following the settling of the precipitate, the supernatant solution was tested with a few more drops of barium chloride solution to ensure complete precipitation of barium sulfate.



The mixture was covered with a clock glass and kept hot for 30–40 minutes.

A fine-porosity sintered glass crucible was used as a filter. The crucible was weighed, and the student filtered the barium sulfate suspension through the glass filter using a water vacuum pump. The precipitate was washed with hot water and finally dried with ethanol washes. After vacuum drying, the crucible was placed in a desiccator before weighing. The results of the gravimetric analysis are given below.

Mass of sintered glass filter = 20.456 g

Mass of filter + BaSO_4 precipitate = 20.791 g

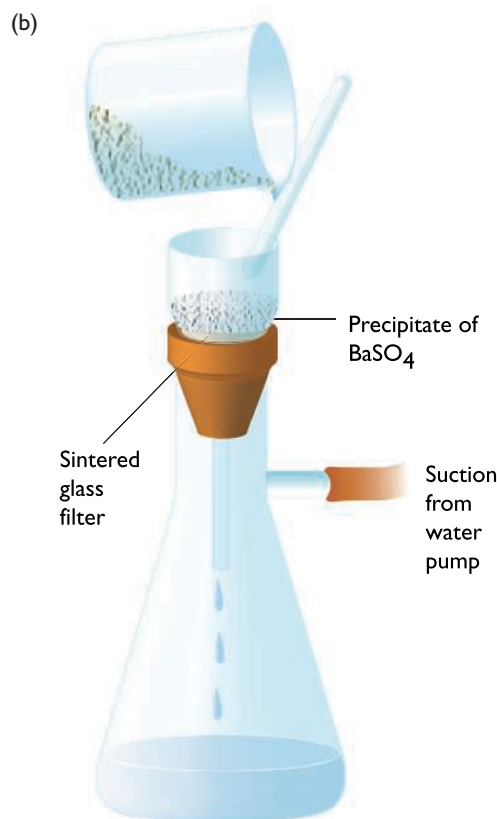


Figure 12.18 (a) Apparatus for precipitation of barium sulfate
(b) Filtration through a sintered glass crucible. Use the information in these diagrams to help you analyse the data.

DATA ANALYSIS

Questions

1. Calculate the mass of barium sulfate precipitated.
2. Calculate the number of moles of barium sulfate precipitated.
3. Write an ionic equation for the precipitation reaction.
4. Calculate the number of moles of sulfate ions present in the fertiliser sample.
5. Calculate the mass of sulfate present in the fertiliser sample.
6. Calculate the percentage by weight of sulfate in the fertiliser.
7. (a) Explain the term *supernatant solution*.
(b) Explain why the supernatant solution was tested with more barium chloride solution.
8. Explain why the precipitate was extensively washed before drying.
9. A 5% (w/v) solution of barium chloride was used in the experiment. Explain how such a solution could be prepared from barium chloride-2-water crystals?
10. Assuming all the sulfate is derived from ammonium sulfate, determine the percentage by weight of ammonium sulfate in the fertiliser.

DATA ANALYSIS

12.4 DATA ANALYSIS

MONITORING LEAD POLLUTION AND USING AAS IN POLLUTION CONTROL

Read and process the following second-hand data, then answer the questions.

Monitoring lead levels in substances used in society

Lead and disease

Lead is a toxic heavy metal. No amount of lead is really safe. In ~200 BC, Dioscorides wrote: '*lead makes the mind give way*'. Over the last 10 000 years the amount of lead in the air has increased 20 times. Lead interferes with the action of particular enzymes in the body. It inhibits the synthesis of haemoglobin and interferes with energy production by cellular mitochondria. Long-term overexposure can cause numerous health problems, including anaemia, nervous system disorders, mental retardation, kidney disease and decreased fertility. Muscle pain, mid-abdominal pain, convulsion and nausea are some symptoms of acute lead poisoning. Only 2 mg of lead can be excreted by the kidneys or through the intestine per day. Excess lead accumulates in the bones and teeth where it replaces the natural calcium.

Leaded paints and young children

Lead has been recognised as a major cause of illness in children and babies living in old homes that have been painted using lead-based paints. These leaded paints often contained up to 50% lead. Leaded-paint dust and flakes may be inhaled or ingested by young children. Young children who crawl along the floor are more likely to get lead dust on their hands and then into their mouths. Such high-lead paints were banned in 1972. The maximum amount of lead in paints is now set at 0.25%.

Other sources of lead in the environment

Apart from leaded paints, lead is present in our environment in other substances, including

contaminated drinking water from lead pipes or solder, car batteries, automobile enamel paints, roof flashing and industrial emissions. Drinking water should have less than 0.01 ppm (10 ppb) of lead (*NHMRC Australian Drinking Water Guidelines*). Lead may also be present in the air as aerosols due to smelting of lead ores (e.g. galena, PbS). In Broken Hill there is a high lead concentration of lead dust in the environment due to mining and smelting. Lead compounds (e.g. tetraethyl lead) were added to petrol in the past in order to improve engine performance. Much of this lead was expelled into the air in the exhaust gases. Since 1986, new cars have been designed to use unleaded petrol. The use of leaded petrol in older cars was discontinued in Australia in 2002.

Recommended blood lead levels

The recommended target for blood lead levels in Australia is < 0.1 ppm. At least 5% of Australian children had levels higher than 0.1 ppm in surveys carried out at the end of the twentieth century. This target lead level can only be achieved by ensuring that there is minimal contamination of our environment with lead, and that existing contamination is cleaned up.

Monitoring lead levels

Measuring and monitoring lead levels in blood (or urine) are important in communities where lead pollution may be a recognised problem. Because lead levels in blood are normally in the parts-per-million range, instrumental rather than 'wet' methods are used as they are more sensitive.

Graphite furnace atomic absorption spectrometry (GFAAS) is a common method used to analyse lead levels in blood. This type of AAS is selected as it is fully automated, allows multiple replications and large sample numbers, as well as being very accurate and reliable. GFAAS is preferable to flame AAS as it requires much smaller volumes of blood for lead detection, and it suffers fewer problems with interference from other materials in the blood. GFAAS is also used to measure lead levels in soil samples, paint and drinking water. The results are analysed and compared with EPA guidelines for safe lead levels.

DATA ANALYSIS

A disadvantage of the AAS technique is its relative lack of portability. Other instruments such as ion selective electrodes (ISE) or X-ray fluorescence analysers (XRF) are increasingly used as they are more portable and allow analyses to be done in the field. XRF analysers are capable of analysing simultaneously for a number of elements in the samples being investigated. XRF analysers are also non-destructive and so can analyse samples of paint, dust and soil for heavy metal contamination without destroying the samples.

Ion selective electrodes are galvanic half-cells that register potential differences that are related to ion or dissolved gas concentration. pH glass electrodes are examples of ISEs. The technology is rapidly evolving and polymer-membrane-based ISEs have been developed. Ion selective electrodes rapidly measure the concentration of specific ions in water solution. Different ISEs are used for different metals. In the case of lead measurements, the electrode is first calibrated using standard solutions containing lead ions. This data is displayed on the computer screen as a calibration graph. The unknown sample is then analysed and the computer uses the calibration graph to determine the lead concentration in the unknown.

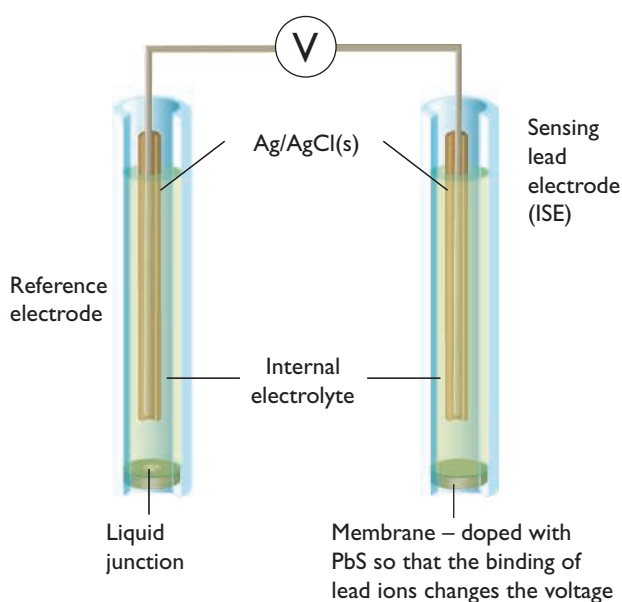


Figure 12.19 A lead ion selective electrode is very useful for field analysis of water samples.

The use of ion selective electrodes to measure the concentration of ions in aquatic environments offers some advantages over other methods. Apart from the obvious portability, these advantages include low setting-up costs and low interference from other components of the sample. In practice, ISEs can detect ions in concentrations as low as 10^{-5} mol/L (e.g. 2 ppm Pb^{2+}) although with suitable buffering this limit can be lowered to 10^{-10} mol/L. Although their accuracy and sensitivity is not as great as AAS, their other features make them useful analytical tools.

Question

Assess the need to monitor levels of lead ions in substances used in society and describe appropriate technologies that can be used to perform such measurements.

Using AAS in pollution control

The Department of Environment and Conservation monitors our air and water to ensure that pollution is kept under control. Any risk assessment of environmental pollutants requires reliable measurements of pollutant concentration. Natural background levels of various materials, including heavy metals in pristine environments, must be established to create a baseline level for comparison. People living in industrialised areas or mining areas are particularly at risk from air and water pollution. AAS is a technique that can be used to analyse for the presence of metal ions, including heavy metals such as lead, mercury and cadmium. Gravimetric or volumetric techniques are not suitable as they are insufficiently sensitive to detect low levels of metal pollutants. AAS is an automated procedure that is easy to use provides rapid results.

Collecting samples

In air monitoring, particulates are collected onto nucleopore filters, and gases are cryogenically filtered and thermally desorbed. In water monitoring, the water samples are filtered through a 0.45 micron membrane filter. Any particulate (colloidal) matter caught by the filter is collected and dissolved in nitric acid to release any metal ions. Dust on surfaces may also contain heavy metals. The dust is removed using a moistened gauze wipe and digested using nitric acid. Heavy metals in soils,

DATA ANALYSIS

sediments and foods are extracted using nitric acid digestion followed by filtration and dilution. The solutions that are prepared are systematically diluted until they are in the same range as the standards for each metal used in AAS analysis. For each metal in turn, the standards are aspirated into the AAS and their absorbances are read. The unknowns follow, and the concentration of the specific metal is interpolated from the calibration graph. The procedure is repeated with new hollow cathode lamps for all metals to be analysed.

Requirements

In order for an instrumental method to be useful in monitoring metals for pollution control, it must satisfy the following requirements:

- relatively cost effective
- scientifically valid
- high sensitivity
- easy to use and readily available.

Only AAS and ICPMS (inductively coupled plasma mass spectrometry) meet all these requirements currently, but other technologies such as ISE (ion selective electrodes) are making rapid progress. ICPMS technology has superiority over AAS as multiple elements can be sampled in one run and there is less interference from other components of the sample. Graphite furnace AAS sampling rates are also slow.

Limitations

AAS data on heavy metals is limited by the different sensitivities or detection limits for each metal.

Typical detection limits for common heavy metals using graphite furnace AAS are listed below.

Source	Metal	Detection limit
In water	cadmium	0.2 ppb
	lead	1 ppb
	mercury	0.05 ppb
In air	cadmium	0.0003 ng/m ³
	lead	0.05 ng/m ³
	mercury	21 ng/m ³

Environmental laboratories that use AAS to monitor samples for heavy metals need to publish these detection limits, rather than merely stating that the samples had zero or undetectable levels of the

pollutant. This is important, as natural background or baseline heavy metal concentrations may be similar to the detection limits for the technology used. In order to make judgements as to whether a mining company is polluting the environment with heavy metals, it is important to know the baseline levels for the area.

Monitoring heavy metal pollution

AAS testing is routinely used in monitoring heavy metal pollution. Heavy metals are highly toxic to animal life. They can enter the food chain at various points and accumulate in human tissue. It is essential that heavy metal levels are monitored to ensure public health is not compromised.

Air samples are routinely collected in various areas where smelters are located, such as Whyalla, Port Pirie and Port Augusta. In addition there are targeted metropolitan sites (e.g. Blacktown, Wollongong, Rozelle, Newcastle) and instrumental techniques such as GFAAS and ICPMS are used to monitor heavy metal aerosols. In the case of lead, air samples are collected over a 6-day (24 hour) cycle before AAS analysis. Results are then compared with the Australian and world standards. Typical 24-hour results in a 1996–2001 study of the Sydney–Newcastle–Wollongong region measured lead levels of 30 ng/m³. These levels are well below the ambient air goal of 500 ng/m³ as recommended by the World Health Organization.

In similar fashion our local waterways are routinely sampled to detect changes in heavy metal ion concentrations that could affect humans and aquatic life. Chemists who are employed in mining and industry must ensure that the concentrations of heavy metals in emissions and effluents do not exceed Department of Environment and Conservation guidelines. AAS data can help environmental chemists offer the appropriate advice to government agencies about suitable actions to prevent further contamination of contaminated riverbeds by heavy metals. These studies have shown that the very high lead levels in sediments in various bays in Sydney Harbour and the Parramatta river (e.g. Homebush Bay and Rozelle Bay) are caused by polluted discharges from stormwater canals.

Question

Evaluate the effectiveness of AAS in pollution control.