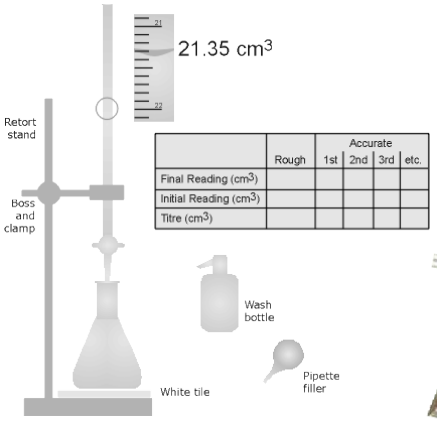
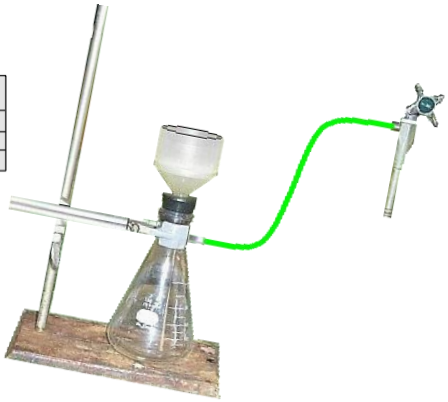
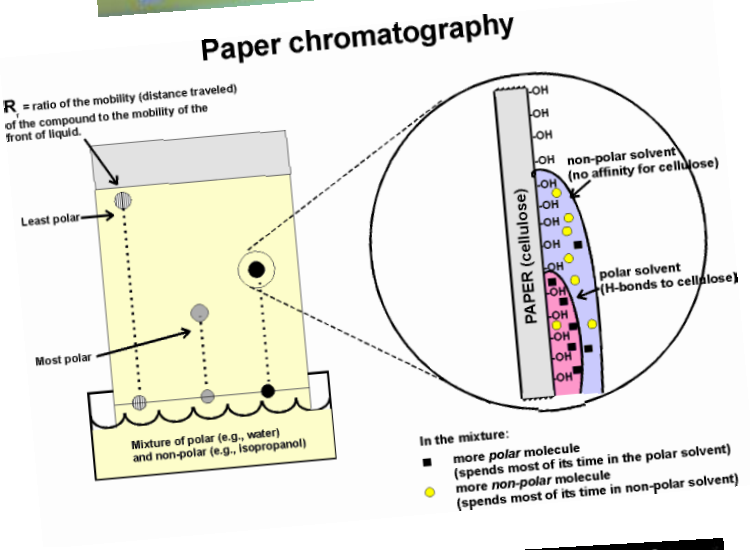
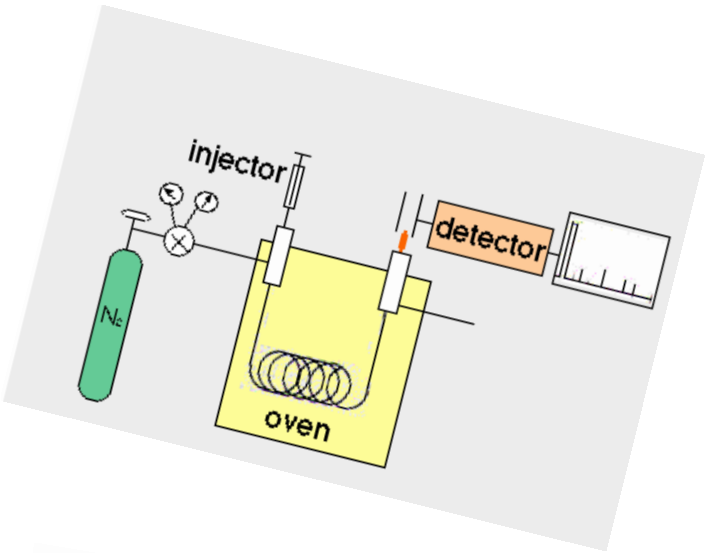
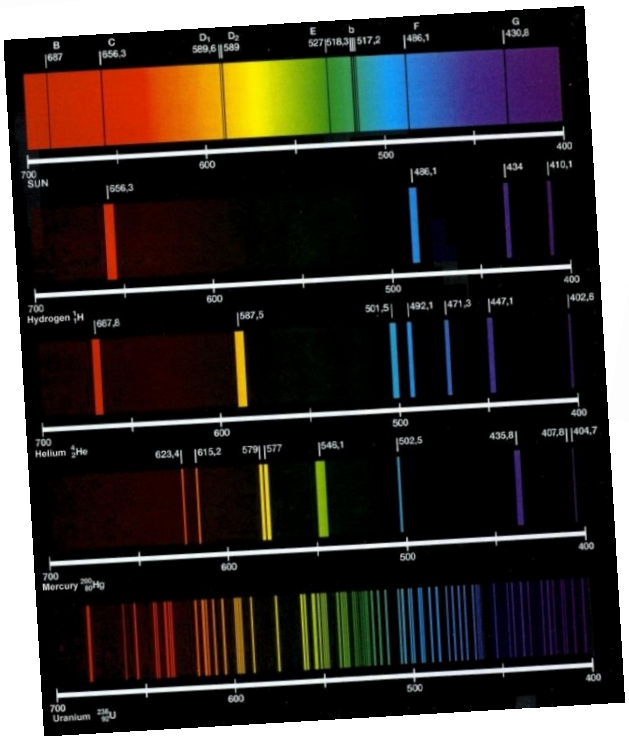
Year 12 Chemistry
Unit 3
Area of Study 1 – Chemical Analysis

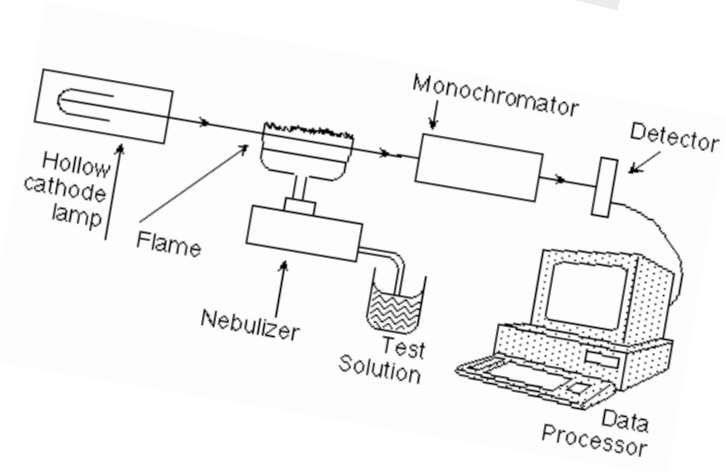












Valence Table of Common Ions

Positive ions (cations)					
+1		+2		+3	
Hydrogen	H^+	Magnesium	Mg^{2+}	Aluminium	Al^{3+}
Lithium	Li^+	Calcium	Ca^{2+}	Chromium (III)	Cr^{3+}
Sodium	Na^+	Barium	Ba^{2+}	Iron (III)	Fe^{3+}
Potassium	K^+	Zinc	Zn^{2+}		
Silver	Ag^+	Copper(II)	Cu^{2+}		
Copper(I)	Cu^+	Mercury (II)	Hg^{2+}		
Ammonium	NH_4^+	Iron (II)	Fe^{2+}		
		Nickel (II)	Ni^{2+}		
		Tin (II)	Sn^{2+}		
		Lead (II)	Pb^{2+}		
Negative ions (anions)					
-1		-2		-3	
Hydroxide	OH^-	Oxide	O^{2-}	Nitride	N^{3-}
Hydrogen Sulfide	HS^-	Sulfide	S^{2-}	Phosphate	PO_4^{3-}
Hydrogen sulfite	HSO_3^-	Sulfite	SO_3^{2-}		
Hydrogen sulfate	HSO_4^-	Sulfate	SO_4^{2-}		
Hydrogen carbonate	HCO_3^-	Carbonate	CO_3^{2-}		
dihydrogen phosphate	$H_2PO_4^-$	Hydrogen phosphate	HPO_4^{2-}		
Nitrite	NO_2^-	Dichromate	$Cr_2O_7^{2-}$		
Nitrate	NO_3^-	Chromate	CrO_4^{2-}		
Acetate	CH_3COO^-	Thiosulfate	$S_2O_3^{2-}$		
Fluoride	F^-				
Chloride	Cl^-				
Bromide	Br^-				
Iodide	I^-				
Permanganate	MnO_4^-				

Solubility Tables for Common Ionic Compounds

ANION	CATIONS FORMING SOLUBLE COMPOUNDS	CATIONS FORMING INSOLUBLE COMPOUNDS
nitrates	all	—
chlorides bromides iodides	most	Ag^+, Pb^{2+} ($PbCl_2$ is moderately soluble in hot water)
sulfates	most	Ba^{2+}, Pb^{2+} (Ag_2SO_4 and $CaSO_4$ are slightly soluble)
carbonates	Na^+, K^+, NH_4^+	most
phosphates	Na^+, K^+, NH_4^+	most
sulfides	Na^+, K^+	most (MgS, CaS, BaS, Al_2S_3 and Fe_2S_3 decompose in water)
hydroxides and oxides	Na^+, K^+, Ba^{2+} (ammonium oxide and ammonium hydroxide do not exist)	most ($Ca(OH)_2$ is slightly soluble)

High Solubility	Low Solubility
Compounds containing the following ions are generally soluble in water • Na^+, K^+, NH_4^+, NO_3^-, CH_3COO^- • Cl^-, Br^-, I^- (unless combined with Ag^+ or Pb^{2+}) • SO_4^{2-} (except $PbSO_4$ and $BaSO_4$; Ag_2SO_4 and $CaSO_4$ are slightly soluble	Compounds containing the following ions are generally insoluble unless combined with Na^+, K^+or NH_4^+ • CO_3^{2-}, PO_4^{3-}, S^{2-} • OH^- (unless combined with Ba^{2+} and Sr^{2+}; $Ca(OH)_2$ is slightly soluble.)

The Mole

What is a mole?

How many atoms or molecules are there in a mole?

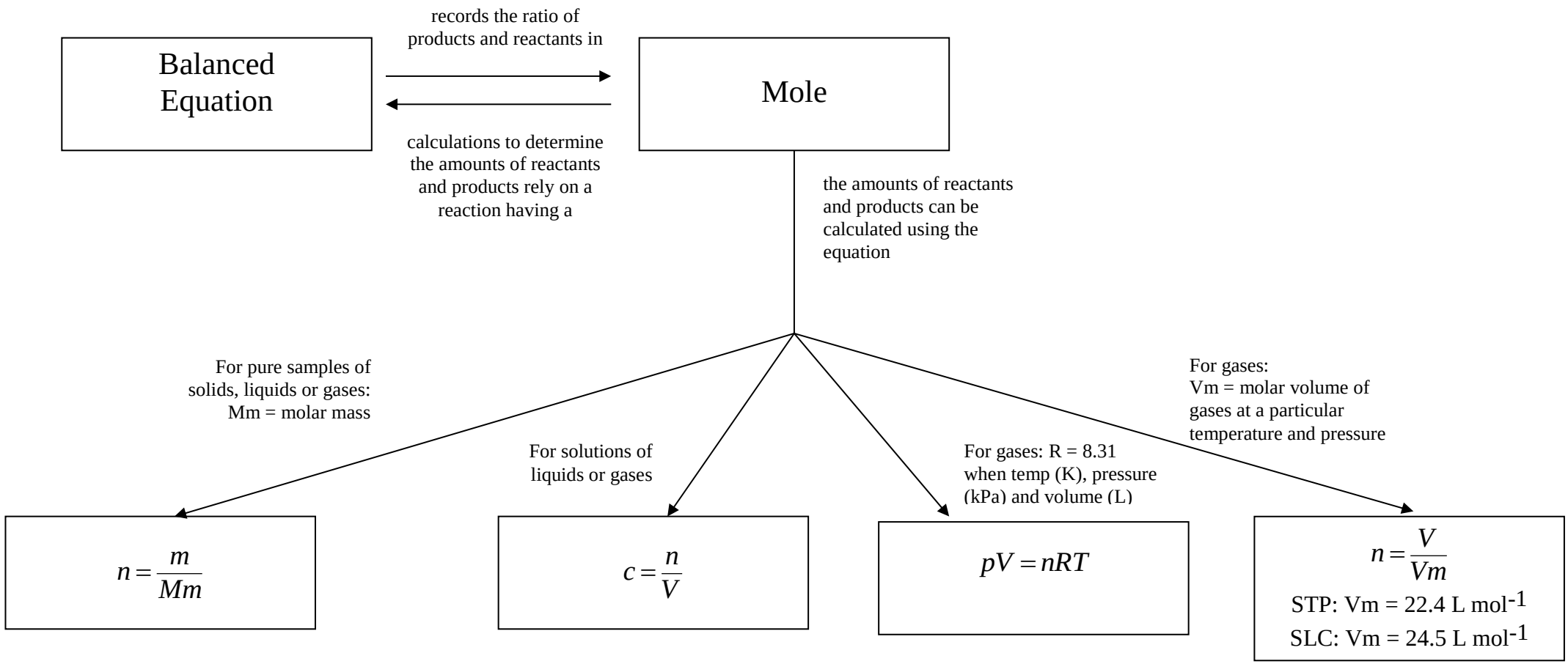
What is Avogadro's Number?

Consider the information that follows and then explain why do we measure chemicals in mole?
The largest element Caesium (Cs) has an atomic diameter of 0.000 000 5 mm, the masses of protons and neutrons are approximately 1.67×10^{-24} g and the mass of an electron is approximately 9.11×10^{-28} g.

Complete the table assuming that there is 1 mole of each compound or molecule.

compound	elements	no. of mole of each element
O_2		
H_2O		
$CuSO_4$		
$C_6H_{12}O_6$		
$Fe(NO_3)_2$		
$Fe(NO_3)_3$		
$K_2Cr_2O_7$		
$Na_2S_2O_3$		

Stoichiometry Concept Map



Mass Stoichiometry – Problem Solving

Key Concepts

- A molecular formular tells you how many atoms of each element there are present in a compound
- An empirical formula is the simplest whole number ratio that can be obtained from a molecular formula

Gravimetric Analysis

Key Concepts

- Gravimetric Analysis is a process that isolates a particular ion, element or compound of interest in a pure form from a mixture
- Gravimetric Analysis is a quantitative procedure that is used to determine the % by mass of that ion, element or compound in the original mixture
- Gravimetric Analysis relies upon the different solubilities of ions in solution

The practical method for a water soluble ion usually involves the following steps:

(i) take a sample of the substance under investigation and weigh it – record the mass
(ii) make a solution of the experimental mixture in water
(iii) filter off everything that is insoluble and discard it
(iv) add a second ionic species that will selectively form a precipitate with the ion under investigation
(v) filter off the precipitate and wash it with water
(vi) dry the precipitate to remove all water and
(vii) weigh the precipitate – record the mass.

Why dry the precipitate?
To determine the mass of the precipitate only.

How do you dry the precipitate?
Place the precipitate in an oven at 110 °C (above the boiling point of water) and weigh it until the mass is constant ie. dry, weigh, dry, weigh, etc.

Calculating the percentage, by mass, of the ion or compound.

To be able to do this you need to know:

(i) the mass of the sample under investigation
(ii) the molecular formula of the precipitate that you have formed and
(iii) the mass of the precipitate

Assumptions that are made.

(i) that the precipitate is absolutely pure and true to its molecular formula
(ii) that all of the ion, element or compound of interest has been precipitated from its solvent
(iii) no precipitate has been lost during the experimental procedure
(iv) that the precipitate is 100% dry

2 Exercise

Gravimetric analysis of chicken soup

Purpose

To determine the amount of salt in a particular product by gravimetric analysis.

Procedure

Excessive intake of salt has been linked to increased blood pressure and heart disease. Many fast foods are high in salt.

A 14.962 g sample of powdered chicken soup was mixed with approximately 100 mL of de-ionised water and stirred thoroughly. The mixture was filtered and the residue washed with more de-ionised water. The filtrate was made up to 250.0 mL in a volumetric flask. A 20.00 mL aliquot of this stock solution was pipetted into a conical flask. An excess of silver nitrate solution was then added.

The chloride ions present in the aliquot of stock solution were precipitated as silver chloride. The precipitate was filtered, dried overnight in an oven and weighed. The mass of silver chloride was 0.246 g.

Part A—Calculation of sodium chloride concentration

1 Calculate the amount, in mol, of silver chloride precipitated.
2 Determine the amount of sodium chloride in a 20.00 mL aliquot of the stock solution.
3 Calculate the amount of sodium chloride in 250.0 mL of stock solution.
4 What mass of sodium chloride was present in the sample of chicken soup?
5 Calculate the percentage by mass of sodium chloride in the powdered soup.

Part B—Determination of the uncertainty in the result

Instruments such as the balance, the burette or the pipette, are engineered to give readings that are guaranteed accurate within a certain range. This uncertainty in mass or volume should be taken into account when estimating the degree to which the result of a particular analysis is uncertain. *For calculations involving multiplication and division, the relative uncertainty in the result of a calculation is equal to the sum of the relative uncertainties in the numbers used in the calculation.*

In this experiment the uncertainties for the equipment used were: top loading balance ±0.002 g, 20 mL pipette ±0.02 mL, 250 mL volumetric flask ±0.2 mL.

Results

1 Complete Table 2.1.

Table 2.1 Uncertainty of results

Measurement	Uncertainty	Relative uncertainty
Mass of soup (14.962 g)	±0.002 g	$\pm\frac{0.002}{14.962} = \pm 0.00013$
Volume of stock solution (250.0 mL)		
Aliquot of stock solution (20.00 mL)		
Mass of precipitate (0.246 g)		

2 Calculate the total of the relative uncertainties.
3 Calculate the uncertainty of your answer to Question 5 in Part A.
(Uncertainty of answer = Total of relative uncertainties × Answer).

Practical Gravimetric Analysis

Theory

Sulfate is a soluble form in lawn fertiliser so that it can easily dissolve into water and by taken up by the plant. To determine how much sulfate is in a sample of lawn fertiliser we follow gravimetric analysis:

1. Filter off the insoluble components and discard
2. Take the filtrate (clear liquid which will contain the sulfate ions)
3. Add an ionic substance which will form an insoluble compound (a precipitate) with the sulfate ions
4. Filter off the precicpitate and dry it
5. Weigh the precipitate and determine the mass of sulfate present

The Ionic Equation

$Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \longrightarrow BaSO_{4(s)}$

Some More Terms

Filtrate – the clear liquid left after filtration
Supernatant – liquid lying above the precipitate

Safety

Lab coats, safety glasses and gloves to be worn when handling conc HCl

Solutions, Concentration and Dilution

Key Concepts

- A solution is a mixture of chemicals that forms when a substance (the solute) is dissolved into another substance (the solvent) to form a mixture (the solution).
- There are several ways to measure the concentration of a solution (how much solute there is in a certain quantity of the solution) but the most common measure in chemistry is molarity (M) ie mol L^{-1}
- The relevant equation to measure molarity is $c = \frac{n}{V}$
- When a solution is diluted (more solvent is added but the mole of solute remains the same) – use the equation $c_1V_1 = c_2V_2$
- When two solutions containg a common ion are mixed together the molarity of the final solution for that common ion is determined by calculating the weighted average of the first two solutions

Measures of Concentration (C)

Mass of Solute per Litre of Solution $\mathrm{C} = \frac{\text{mass of solute (g)}}{\text{volume of solution (L)}}$

Example: 5 g of $CuSO_4$ in 100 mL of a solution: $\mathrm{C} = \frac{5\text{g}}{0.1\text{L}} = 50gL^{-1}$

Mole of Solute per Litre of Solution $\mathrm{C} = \frac{\text{mole of solute (mol)}}{\text{volume of solution (L)}}$

Example: 0.25 mol of KI in 2 L of a solution $\mathrm{C} = \frac{0.25\text{mol}}{2\text{L}} = 0.125molL^{-1} = 0.125M$

Other Measures of Concentration

Percentage by Mass (w/w) $\mathrm{C} = \frac{\text{mass of solute (g)}}{\text{mass of solution (g)}} \times 100\%$

Example: 5 g of NaCl in 100 g of a solution = 5% w/w

Percentage by Volume (v/v) $\mathrm{C} = \frac{\text{volume of solute (mL)}}{\text{volume of solution (mL)}} \times 100\%$

Example: 12.5 mL of alcohol in 100 mL of a solution = 12.5% v/v

Percentage Mass/Volume (w/v) $\mathrm{C} = \frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 100\%$

Example: 20 g of sugar in 100 mL of a solution = 20% w/v

Parts Per Million (ppm)

$$\mathrm{C} = \frac{\text{mass of solute (g)}}{\text{mass of solution } (10^6\text{ g})}$$

$$ppm = \frac{g}{10^6 g} = \frac{\mu g}{g} = \frac{mg}{L}$$

Example: 0.4 g of DDT in 10^6 g of a solution = 0.4 ppm

Note: any of these equations can be transposed during problem solving.

Primary Standards and Standard Solutions

What is a standard solution?
Standard solutions are solutions that have very accurately known concentrations.

When do standard solutions become useful?
During the process of volumetric analysis. The point to volumetric analysis is to use a solution with an accurately known concentration (a standard solution) to determine the concentration of an unknown solution.

How are standard solutions prepared?
A standard solution is a solution which is prepared from a solid material (a primary standard), which acts as the solute, and a solvent. To prepare a standard solution you must have a pure sample of the solute that you wish to use. Because the purity of the solute is so important it must have certain useful properties.

The properties of primary standards.
- They must be easily obtained in a high state of purity
- they must be stable when stored ie. they shouldn't react with gases in the air or with water (humidity must not affect a primary standard)
- they should be readily available and cheap and
- they should have a high formula weight (be a largish compound) to minimise errors in weighing.

The laboratory preparation of a standard solution.
- The primary standard must be accurately weighed (when the molecular mass of a compound is large, small errors in weighing the mass of that compound translate to very small errors in the amount of mole – remember that the mole of any reagent is the quantity that has an impact on the stoichiometry of a reaction)
- the primary standard is then added to a volumetric flask and dissolved in a solvent – usually distilled water
- volumetric flasks have calibration lines etched onto them which measure volume to within ± 0.25 mL and
- the concentration of this standard solution is then determined by using the equation: **c = n/v**

How is the concentration of an unknown solution determined?
We carefully measure a volume of an unknown solution that we will titrate against a standard solution. To determine the endpoint of reaction between an unknown solution and a standard solution we usually add an indicator. The standard solution is added to the unknown (which is usually put into a conical flask) from a burette. We accurately record the volume of standard solution that we titrate. Then through the use of a stoichiometric equation, and the known volume and concentration of the standard solution that we have titrated, we can determine the concentration of an unknown solution.

Volumetric analysis is one example of quantitative analysis.

Volumetric Analysis - Theory

Key Concepts

- Volumetric Analysis is a process that uses a solution of accurately known concentration (a standard solution) to determine the concentration of an unknown solution
- A primary standard is a compound of known molecular formula that can be maintained in a state of high purity
- A standard solution has its concentration accurately determined by dissolving an accurately measured mass of a primary standard into an accurately measured volume of deionised water, or by "standardising a solution"
- "Standardising a solution" means to determine the concentration of a solution through a reaction such as a titration.
- Acid base indicators are usually weak acids that have a conjugate with a different colour ie. they change colour when the pH of a solution changes

The Properties of Primary Standards

- they must be easily obtained in a high state of purity
- they must be stable when stored ie. they must not react with gases in the air or with water (humidity must not affect a primary standard)
- they should be readily available and cheap and
- they should have a high formula weight (be a largish compound) to minimise errors in weighing ie the accuracy of any standard solution is dependent on how accurately the number of mole of primary standard that is added has been determined (n = m/Mm) – the larger Mm is the smaller the percentage error in weighing.

Recording Titrations

Results

$NaOH_{(aq)} + KH(C_8H_4O_4)_{(aq)} \longrightarrow KNa(C_8H_4O_4)_{(aq)} + H_2O_{(l)}$

Mole ratio 1 : 1 : 1 : 1

$Mm_{(KH(C8H4O4)} =$

Titration Number	1	2	3	4
Mass of $KH(C_8H_4O_4)$				
Mole of $KH(C_8H_4O_4)$				
Mole of NaOH				
Burette Reading (final) mL				
Burette Reading (initial) mL				
Volume of Titre (cm^3)				
Concentration of NaOH				

*Concordant titres are the three that agree best ie. the three titres that are closest in value.

$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$

Mole ratio 1 : 1 : 1 : 1

$C_{(NaOH)} =$

Titration Number	1	2	3	4
Burette Reading (final) mL				
Burette Reading (initial) mL				
Volume of Titre (cm^3)				

*Concordant titres are the three that agree best ie. the three titres that are closest in value.

Determine the average titre for the 3 concordant titres.

$v_{(NaOH)} =$

Year 12 Chemistry
Acids & Bases Revision Quiz

2. A solution of a base when tested with pH paper will give a result
   - A. greater than 7
   - B. less than 7
   - C. equal to 7
   - D. no result

4. The definition an acid is a chemical capable of donating a proton while a base is capable of accepting a proton, was suggested by
   - A. Lavoisier
   - B. Bonsted-Lowery
   - C. Arrhenius
   - D. Davey

6. Assuming acids are proton donors and bases proton acceptors, which of the following underlined species behaves as an acid when added to water?

   A. $\underline{NH_{3(aq)}} + H_2O_{(l)} \rightarrow NH^+_{4(aq)} + OH^-_{(aq)}$

   B. $\underline{HCO^-_{3(aq)}} + H_2O_{(l)} \rightarrow H_2CO_{3(aq)} + OH^-_{(aq)}$

   C. $\underline{HSO^-_{4(aq)}} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + SO^{2-}_{4(aq)}$

   D. $\underline{Na_2CO_{3(s)}} + H_2O_{(l)} \rightarrow HCO^-_{3(aq)} + OH^-_{(aq)} + 2Na^+_{(aq)}$

7. Assuming acids are proton donors and bases are acceptors , which of the following underlined species behaves as a base when added to water?

   A. $\underline{H_3PO_{4(aq)}} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + H_2SO^-_{4(aq)}$

   B. $\underline{NH^+_{4(aq)}} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + NH_{3(aq)}$

   C. $\underline{HSO^-_{3(aq)}} + H_2O_{(l)} \rightarrow H_2SO_{4(aq)} + OH^-_{(aq)}$

   D. $\underline{CH_3COOH_{(aq)}} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$

8. Substances which can act as an acid or base are called
   - A. allotropic
   - B. amphiprotic
   - C. allelomorphic
   - D. anthropomorphic

9. Water is only weakly ionized and the concentration of H^+ ions in pure water at 298^o K is
   - A. 10^{-14} M
   - B. 10^{-7} M
   - C. 10^{-1} M
   - D. 14 M

10. Ions are required to carry an electrical current in an aqueous solution. Which of the solutions below is the poorest electrical conductor?
   - A. $HNO_{3(aq)}$
   - B. $CH_3COOH_{(aq)}$
   - C. $H_2SO_{4(aq)}$
   - D. $KCl_{(aq)}$

13. The formula for the conjugate base of H_2SO_4 is

A. HS^-
B. HSO_4^-
C. SO_4^{2-}
D. SO_3^{2-}

14. The conjugate acid for OH^- is

A. H_2O
B. H^+
C. H_3O^+
D. O^{2+}

15. The conjugate base for NH_3 is

A. NH_4^+
B. NH_4OH
C. OH^-
D. NH_2^-

16. The conjugate acid for HS^- is

A. S^{2-}
B. H^+
C. H_2S
D. H_2S^-

1. Given that pH $= -\log_{10}\{H^+\}$ what is the pH a 0·001 M solution of HCl?

A. 10^{-3}
B. 3
C. 0·001
D. 1

2. The pH of 0·001 M of NaOH is

A. 10^{-3}
B. 3
C. 0·001
D. 11

3. 10 mL of 0·1 M HNO_3 is diluted to 1 litre with pure water. The resulting solution will have a pH of

A. 100
B. 10^{-2}
C. 3
D. 0·001

99.80 g. Comment on the errors that are likely to be present in his measurements. Do the measurements show a high degree of (i) accuracy, (ii) precision?

RECORDING ERRORS

Uncertainty

Instruments are produced to measure within a particular range of values determined by the quality of manufacture. If a measured quantity m has an uncertainty δm, an estimate of the probable range within which the true value of the quantity lies is $m \pm \delta m$. No account is given of the types of errors influencing this range.

For example, a balance weighing to two decimal places may be accurate to within ± 0.01 g. Thus, a 50 gram mass weighed on this balance would have its mass recorded as 50.00 ± 0.01 g; the "true" mass probably lies between 49.99 and 50.01 g.

Table 1.2 shows typical uncertainties in some common laboratory instruments.

Table 1.2

Instrument		Uncertainty
Substitution balance (electric)		± 0.002 g or ± 0.0002 g
Top-loading balance (electric)		± 0.002 g
Multiple-arm balance		± 0.01 g
Pipette		± 0.01 cm^3
Burette		± 0.02 cm^3
Measuring cylinders:	10 cm^3	± 0.1 cm^3
	50 cm^3	± 0.5 cm^3
	100 cm^3	± 0.5 cm^3
	250 cm^3	± 1.0 cm^3
	500 cm^3	± 2 cm^3
	1000 cm^3	± 5 cm^3
Standard flask	250 cm^3	± 0.25 cm^3

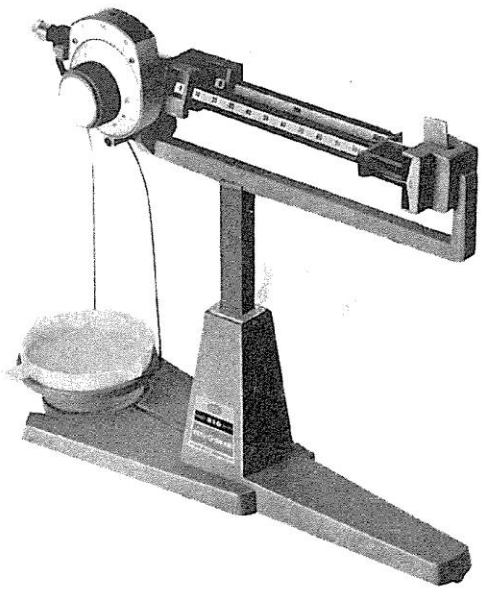


Figure 1.1: A multiple-arm balance: Ohaus "Dial-o-Gram" 310

Fractional uncertainty, $\frac{\delta m}{m}$, and percentage uncertainty, $\frac{\delta m}{m} \times 100\,\%$

If the "true" value of a mass is 100.0 g with a probable uncertainty of 0.1 g, then the fractional uncertainty is $\frac{\text{uncertainty}}{\text{true value}} = \frac{0.1}{100.0}$, the units cancelling.

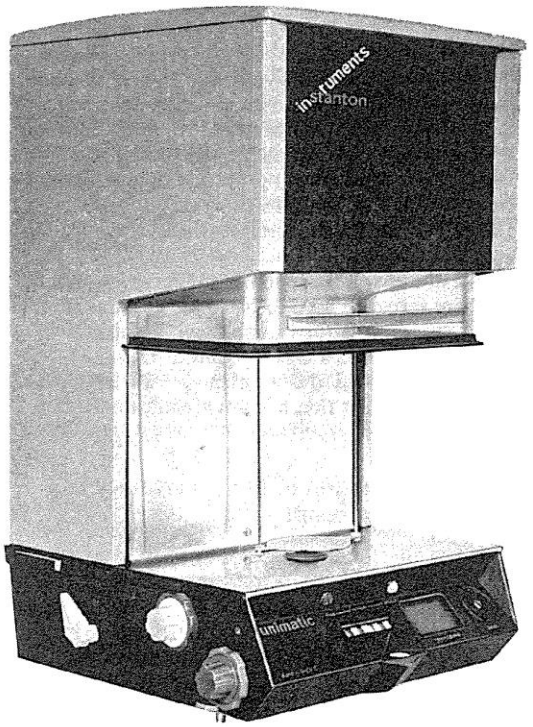


Figure 1.2: An electric substitution balance: Stanton Unimatic

Figure 1.3: A top-loading balance: Oertling TP45

5 Experiment

Preparation of a standard solution

This experiment is also included in *Heinemann Chemistry 2 Student Workbook* as Practical activity 01 Analysis of brick cleaner, Part A.

Duration

20 minutes

Materials

- anhydrous sodium carbonate
- 250 mL de-ionised water
- 250 mL volumetric flask
- weighing bottle or watch glass
- small funnel
- spatula
- dropping pipette
- wash bottle containing de-ionised water
- electronic balance
- paper label or marking pen
- safety glasses

Safety

- Wear safety glasses and a laboratory coat for this experiment.
- Sodium carbonate may irritate eyes and respiratory system.

Purpose

To prepare a standard solution from a primary standard.

Procedure

1 Calculate the mass of anhydrous sodium carbonate (Na_2CO_3) required to make up 250 mL of 0.1 M solution.
2 Weigh out this mass of anhydrous sodium carbonate (within 0.1 g) in a weighing bottle. Record the exact mass of solid used.
3 Use a small funnel to transfer the sodium carbonate, a little at a time, to a 250 mL volumetric flask. Use a wash bottle of de-ionised water to wash traces of sodium carbonate in the weighing bottle and funnel into the flask.
4 Add de-ionised water to the flask until it is almost half full. Stopper and swirl the contents of the flask to dissolve the sodium carbonate.
5 Add more water until the meniscus of the solution is nearly level with the calibration line. Use a dropping pipette to add the final few drops of de-ionised water so that the bottom of the meniscus is exactly level with the calibration line. (Ensure the flask is standing on a horizontal surface and your eye is at the same level as the line.)
6 Shake the flask so that the concentration of the solution is uniform. Label the flask with its contents and concentration and your name.

Theory

Standard solutions have accurately known concentrations and are used in titrations to determine the concentration of a solution of unknown concentration. They can be made by dissolving a measured mass of a primary standard in a known volume of solution. Refer to *Heinemann Chemistry 2*, Chapter 3, for a description of the preparation of standard solutions.

Questions

1 Calculate the concentration, in moles per litre (M L^{-1}), of the sodium carbonate solution.
2 Why is solid sodium hydroxide not used as a primary standard when standard solutions of bases are required?
3 List the properties necessary for a chemical to be used as a primary standard.
4 Identify some of the sources of error associated with this experiment.
5 How would the concentration of the standard solution be affected if the volumetric flask had been rinsed with de-ionised water before use and droplets of water were left in the flask when the sodium carbonate was added?

Experiment 9 – Q.8-10

General questions

8 a How does your answer to Question 7 compare with the manufacturer's claim as to the composition of the brick cleaner?
  b Compare your result with those of other members in your class. Explain why differences arise and how a more accurate result could be obtained.
9 Explain how you would safely clean up spill of about 20 mL of brick cleaner on the floor.
10 With what should the following apparatus be rinsed prior to use in this experiment?
  a volumetric flask
  b burette
  c pipette
  d conical flask

9 Experiment

Analysis of brick cleaner

This experiment is also included in *Heinemann Chemistry 2 Student Workbook* as Practical activity 01 Analysis of brick cleaner, Part B.

Duration

40 minutes

Materials

- 5 mL brick cleaner
- 100 mL approximately 0.1 M standard sodium carbonate solution (The standard solution prepared in Experiment 5 can be used.)
- 250 mL de-ionised water
- methyl orange indicator
- 250 mL volumetric flask
- 4 × 100 mL conical flasks
- small funnel
- 10 mL measuring cylinder
- 20 mL pipette
- pipette filler
- dropping pipette
- burette and stand
- white tile
- electronic balance
- safety glasses
- gloves

Safety

- Wear safety glasses and a laboratory coat for this experiment.
- Brick cleaner contains a high concentration of hydrochloric acid. It is highly corrosive to the eyes and skin and may cause burns. Handle with care. It is an irritant to the respiratory system. Mop up spills immediately, washing them away with copious amounts of water.
- Methyl orange may cause irritation to the skin and eyes. Avoid contact.

Purpose

To use a standard solution (previously prepared) to find the percentage, by mass, of hydrogen chloride (present as hydrochloric acid) in brick cleaner using an acid–base titration.

Procedure

1 Weigh a clean, dry 250 mL volumetric flask and record its mass.
2 Note the hydrogen chloride content of the brick cleaner as specified by the manufacturer. Use a 10 mL measuring cylinder to pour about 5 mL brick cleaner into the volumetric flask, avoiding spillages. Stopper the flask immediately.
3 Reweigh the flask plus contents.
4 Add de-ionised water until the flask is about half full. Stopper the flask and turn it upside down *carefully* several times to mix the solution thoroughly.
5 Add more water to the flask until the meniscus is level with the graduation line. Stopper and mix the solution thoroughly.
6 Use a 20 mL pipette to place 20.00 mL aliquots of standard sodium carbonate solution into four 100 mL conical flasks. Add two to three drops of methyl orange indicator to each conical flask. Set one flask aside to act as a control in colour matching.
7 Fill a burette with the diluted solution of brick cleaner and record the initial level of the solution in the burette to two decimal places.
8 Titrate the sodium carbonate solution with the solution of brick cleaner until the moment when the indicator just shows a permanent colour change from yellow to orange. Record the final burette reading and calculate the volume of the titre.
9 Repeat the titration until you obtain three titres that are concordant (i.e. the smallest of which is no more than 0.1 mL less than the largest).

Theory

Brick cleaner contains concentrated hydrochloric acid as the active ingredient. The acid reacts with the basic components of concrete and so enables concrete to be removed from brickwork. To analyse brick cleaner, a sample is diluted (since the original acid is highly concentrated) and titrated against a standard solution of a base, sodium carbonate.

Refer to *Heinemann Chemistry 2*, Chapters 3 and 4, for descriptions of the principles of volumetric analysis applied to acid–base reactions.

Questions

Calculations

1 Determine the mass of the sample of brick cleaner.
2 Find the average volume of the three concordant titres.
3 Calculate the amount of sodium carbonate, in mol, present in each conical flask.
4 Write an equation for the reaction which occurs between hydrochloric acid and sodium carbonate solution.
5 Calculate the amount of hydrochloric acid, in mol, present in the average titre.
6 Calculate the amount of hydrochloric acid, in mol, present in the volumetric flask.
7 Find the percentage, by mass, of HCl in the brick cleaner.

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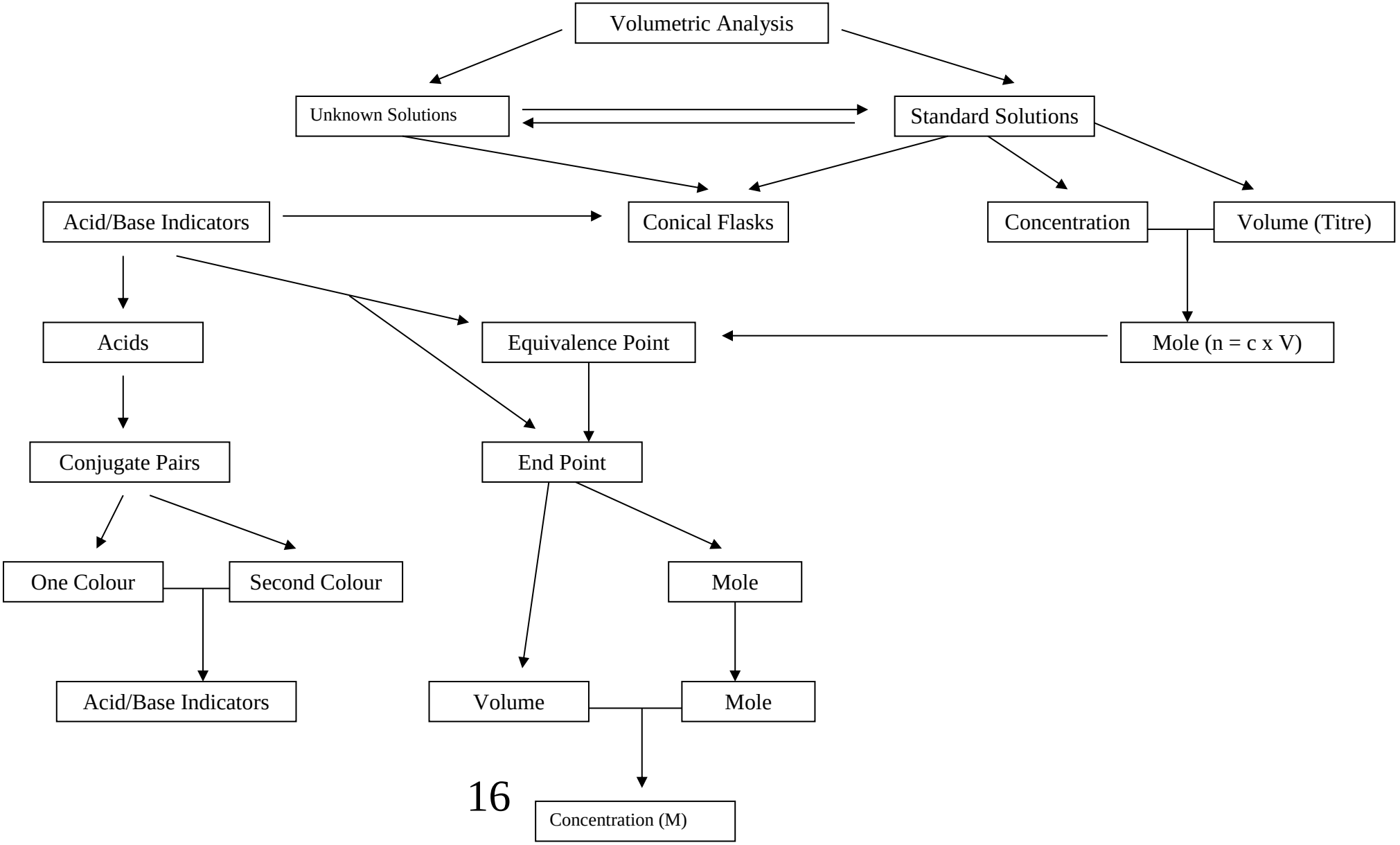
Volumetric Analysis of Acids and Bases – Concept Map

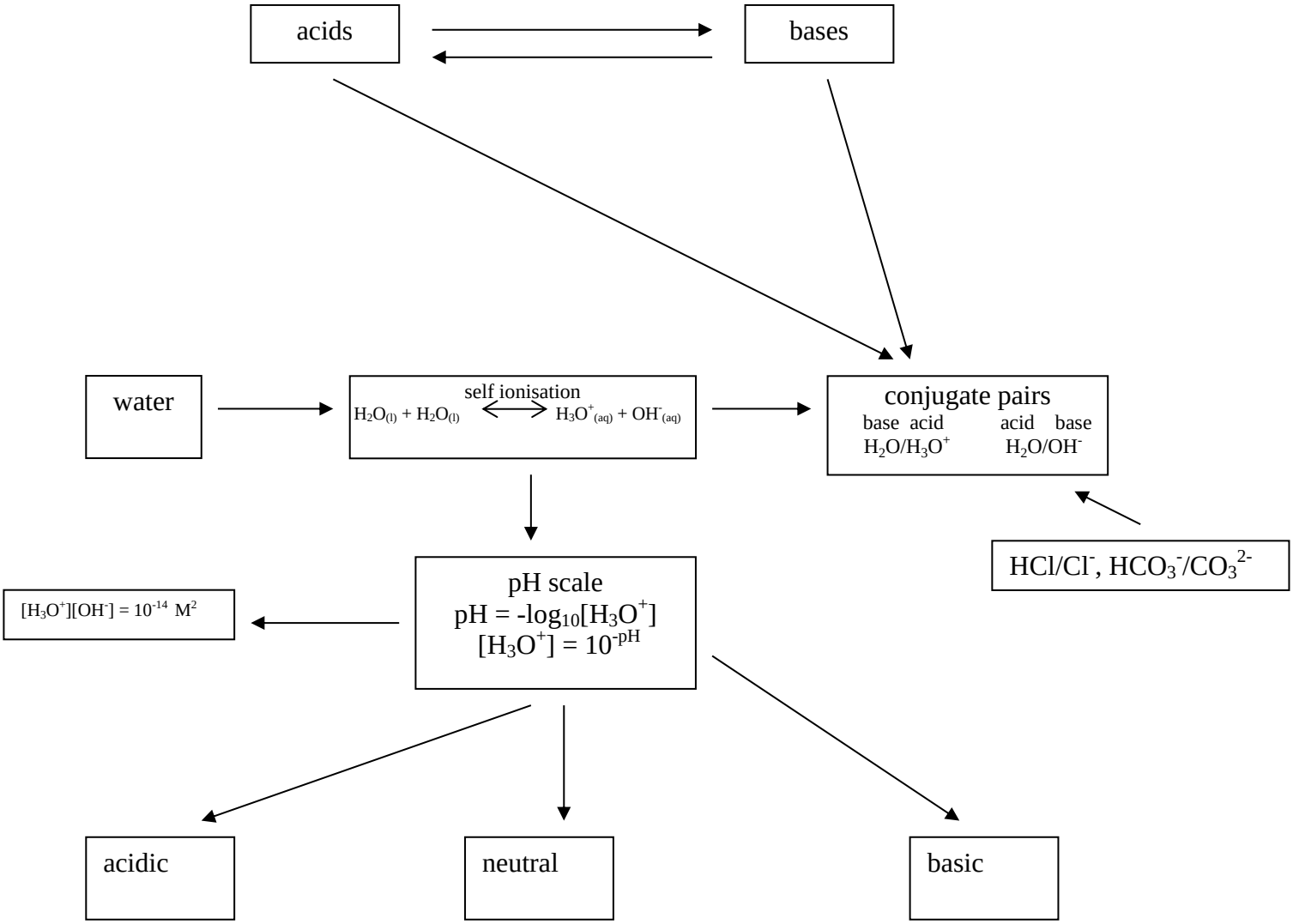


Acids and Bases

Key Concepts

- Acid/base reactions involve an exchange of protons
- Acids and bases have conjugate pairs: the conjugate base of an acid will have the same molecular formula minus a proton (HCl/Cl^-), the conjugate acid of a base will have the same molecular formula plus a proton (OH^-/H_2O)
- An acid has a charge 1 greater than its conjugate base
- Water molecules can act as acids or bases ie. water is said to self ionise according to the equation: $H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$
- The pH scale is a measure of the concentration of $H_3O^+_{(aq)}$ ions in a solution

Acids & Bases Concept Map



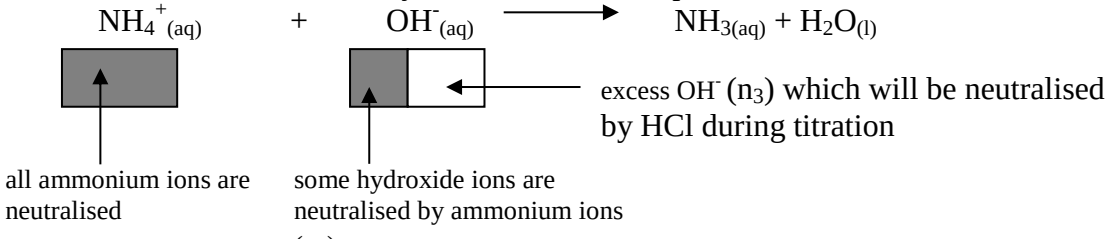
Back Titrations - Theory

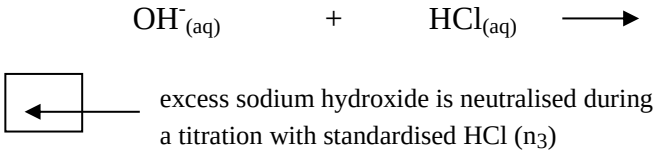
Key Concepts

- Back Titrations are only performed through necessity eg. if the chemical you are studying is prone to evaporate during titration or if it is fairly unreactive and does not provide a clear end-point for the titration
- The usual scenario for a back titration involving a weak acid or base is:
  - -the weak acid or base is neutralised with an excess of strong acid or base
  - -the excess of strong acid or base is then titrated against another strong acid or base – this titration will have a very clear end-point
- Back titrations may also be used to determine the amount of a product that is formed from a reaction:
  - -an excess of a reactant is added to a chemical under investigation
  - -a product is formed that is then titrated against a standard solution
  - -the amount of product formed from the first reaction is then used, with reference to a balanced chemical equation, to determine the amount of the chemical that is under investigation

Back Titration – an example (Q.26 on p.46)

Note that the total amount of sodium hydroxide in the example below will be listed as n_1.





$m_{(\text{fertiliser sample})}$ = $v_{(\text{fertiliser solution})}$ = $v_{(\text{fertiliser solution in reaction})}$ =

$c_{(NaOH)}$ = $v_{(NaOH)}$ = $n1_{(NaOH)}$ =

$c_{(HCl)}$ = $v_{(HCl)}$ = $n_{(HCl)}$ =

a.

b.

c.

d.

e.

Oxidation & Reduction

- **Oxidation** is the loss of electrons – this reactant is **oxidised** – this reactant is said to be acting as the **reductant** because it is handing electrons over to another reactant
- **Reduction** is the gain of electrons – this reactant is **reduced** – this reactant is said to be acting as the **oxidant** because it is taking electrons from another reactant

How can we remember these confusing terms?
Through the use of acronyms.

AN	Anode	
OIL	Oxidation Is Loss	of electrons
RIG	Reduction Is Gain	of electrons
CAT	Cathode	

Oxidant Undergoes Reduction → O U R

Reductant Is Oxidised → R I O

Oxidation Numbers

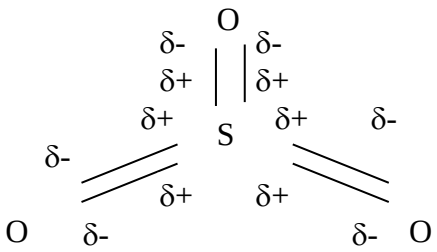
An artificial device that determines the charges on individual atoms if there was a complete transfer of electrons from the element with low electronegativity to the element of higher electronegativity.

Examples: (each example has included dipoles – each line represents a pair of shared electrons and therefore each line represents one partial charge).

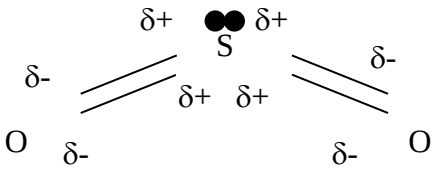
(i) Record the oxidation numbers of each element beneath each diagram.

(ii) Draw in the electron pairs in each bond and clearly indicate their positions within the bonds.

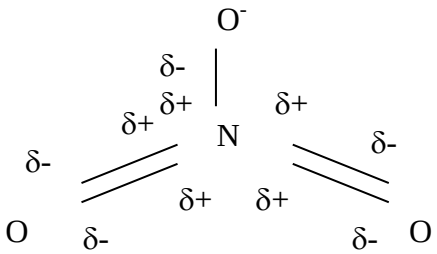
SO_3



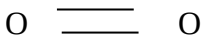
SO_2



NO_3^-



O_2



General Rule: -an increase in O.N = oxidation
-a decrease in O.N = reduction

For a reaction to be classified as redox there must be a change in oxidation state of at least one element.

KOHES – writing redox equations for acidic solutions

K – balance the key element
O – balance O by adding moles of H_2O to the side lacking O
H – balance H by adding moles of H^+ ions to the side lacking H
E – balance the charge by adding moles of e^- to the side with the highest charge in order to have both sides equal in charge
S – include states of matter

Note: these rules apply only to reactions in acidic solutions.

Redox Titration – Practical

Key Concepts

- Some redox titrations do not require the use of an indicator because one of the reactants may be a different colour in its oxidised state than in its reduced state
- Some metal cations have a different colour when they are in different oxidation states eg. $Cr_2O_7^{2-}$(orange) $\longrightarrow$ Cr^{3+}(green), Cr's oxidation state has changed from +6 to +3, Cr has been reduced and there is an obvious colour change

A Breathalyzer
Breathalyzers detect alcohol on the basis of a redox reaction:

$$\underset{\text{(orange)}}{Cr_2O_7^{2-}} + 14H^+ + 6e^- \longrightarrow \underset{\text{(green)}}{2Cr^{3+}} + 7H_2O$$

$$CH_3CH_2OH + H_2O \longrightarrow CH_3COOH + 4H^+ + 4e^-$$

If you check the oxidation numbers above you will see that Cr has been reduced while C has been oxidised. The colour change that we observe is due to the reduction of Cr.

If the above reaction was performed as a titration would you need to use an indicator? Explain.

_____

_____

_____

Telling the Difference Between an Acid/Base Reaction and a Redox Reaction
During a redox reaction the oxidation states of reactants changes – it is enough to check the oxidation state of one reactant to identify an oxidation/reduction reaction.

$$HCl + H_2O \longrightarrow Cl^- + H_3O^+$$

$$OCl^- + 2I^- + 2H^+ \longrightarrow I_2 + Cl^- + H_2O$$

20 Experiment

Determination of sulfur dioxide content in wine

Purpose

To determine the mass of sulfur dioxide in wine by performing a redox titration.

hi com.au weblink

Procedure

1 Record the brand of wine to be analysed.
2 Use a pipette to transfer a 20.00 mL volume of wine to each of three 250 mL conical flasks.
3 Add about 12 mL 1 M sodium hydroxide solution to each flask and allow the flasks to stand for 15 minutes.
4 Fill a burette with standard iodine solution. Record the initial burette reading and the concentration of the solution.
5 To one flask, add about 10 mL 2 M sulfuric acid and 1–2 mL starch indicator solution. Immediately titrate the mixture with the iodine solution. The end point occurs the moment the mixture turns permanently blue. Record the final burette reading.
6 Repeat step 5 using the two other flasks.

Theory

On exposure to the air for several hours, wine acquires a 'vinegary' taste due to the oxidation of ethanol to ethanoic (acetic) acid. Oxidation is caused by bacteria present in the wine as well as by direct reaction of ethanol with oxygen in the atmosphere.

The problem can be reduced by the addition of sulfur dioxide which acts as a reductant and also inhibits the action of the bacteria. Reactions also take place within the wine to 'fix' the sulfur dioxide in the form of 'bisulfite addition compounds'. Sodium hydroxide solution is added to the aliquots of wine to convert these bisulfite addition compounds to sulfite ions. Then, when sulfuric acid is added, sulfite and hydrogen sulfite ions are converted to sulfur dioxide in aqueous solution. The titration must be performed quickly to reduce the loss of sulfur dioxide gas.

Volumetric analysis involving redox reactions is described in *Heinemann Chemistry 2*, Chapter 5.

Questions

Calculations

1 Calculate the average titre of iodine solution.
2 Calculate the amount of iodine, in mol, in the average titre.
3 The half equations for the titration reactions are:

$$SO_2(aq) + 2H_2O(l) \rightarrow 3H^+(aq) + HSO_4^-(aq) + 2e^-$$
$$I_2(aq) + 2e^- \rightarrow 2I^-(aq)$$

Write an ionic equation for the redox reaction that occurs during the titration.
4 Calculate the amount of sulfur dioxide present in each 20.00 mL aliquot of wine.
5 Calculate the amount of sulfur dioxide that would be present in 1 L of the wine.
6 Calculate the mass of sulfur dioxide that would be present in 1 L of the wine.

General questions

7 Does the sulfur dioxide content of this sample of wine fall within the legal limit of 250 mg^{-1}?
8 How would the volume of iodine solution required in the titration be affected if sodium hydroxide is not added to the wine? Explain your answer.
9 If you were to add the sulfuric acid to all three flasks containing wine at the same time, instead of adding it to each sample just before it is titrated, you would be unlikely to obtain concordant results. Why?

Duration

45 minutes

Materials

- 60 mL white wine
- 40 mL 1 M sodium hydroxide solution
- 100 mL standard iodine solution (approximately 0.005 M)
- 30 mL 2 M sulfuric acid
- starch indicator
- 3 × 250 mL conical flasks
- 20 mL pipette
- pipette filler
- 25 mL measuring cylinder
- burette and stand
- small funnel
- white tile
- safety glasses

Safety

- Wear safety glasses and a laboratory coat for this experiment.
- Iodine solution stains skin, clothing and bench surfaces.
- Sodium hydroxide and sulfuric acid solutions are corrosive.

Introduction to Chromatography
(Thin-Layer & Paper Chromatography: text ref.62-64)

Key Concepts

- Chromatography is a form of qualitative analysis that separates mixtures of chemicals (certain types of chromatography are quantitative)
- Chromatography works on the principle that all chemicals interact to some degree, and that different chemicals interact to differing degrees
- Chemical interaction essentially means "bonding"
- In chromatography chemicals in a mixture bond to a stationary material and to a mobile solvent – the degree of bonding to the stationary phase, and to the mobile material, will ultimately separate chemicals from a mixture

Separation of Components in Chromatography

The components of in a mixture separate according to

- how strongly they "adsorb" to the stationary phase and
- how readily they dissolve into the mobile phase (the solvent)

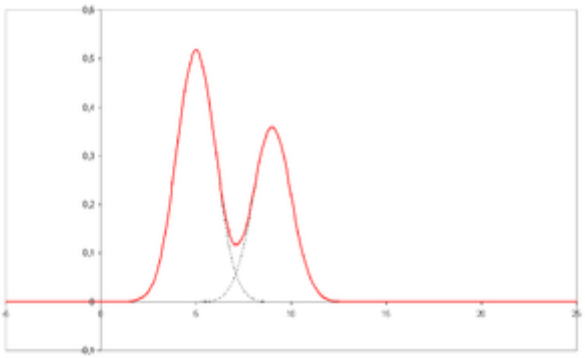
The Process of Chromatogtraphy

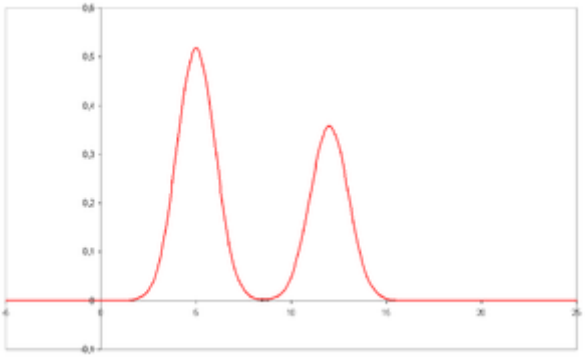
- Separation is due to: the **size** of molecules under investigation & the **polarity** of these molecules
- Molecules under investigation adsorb (Adsorption, the binding of molecules or particles to a surface, must be distinguished from *absorption*, the filling of pores in a solid. The binding to the surface is usually weak and reversible.) to a stationary phase & dissolve into a mobile phase.
- This means that there is a chemical reaction between the molecules under investigation and both the mobile and stationary phases ie. bonding to both. The nature of bonding is therefore critical to separation and hence the relative polarities is critical.
- Like bonds to like – this means that a polar stationary phase will result stronger adsorption from polar molecules and an increase in retention factors and times. If the stationary phase is non-polar retention of non-polar molecules is increased. The polarity of the stationary phase chosen works in a similar way eg. polar solvents dissolve polar molecules more readily and decrease retention time for these. Non-polar solvents will more readily dissolve non-polar molecules and hence decrease their retention times.
- **The same principles apply to all types of chromatography.**

Some Terminology Relevant to Chromatography

- The **analyte** is the substance that is to be separated during chromatography.
- **Analytical chromatography** is used to determine the existence and possibly also the concentration of analyte(s) in a sample.
- A **bonded phase** is a stationary phase that is covalently bonded to the support particles or to the inside wall of the column tubing.
- A **chromatogram** is the visual output of the chromatograph. In the case of an optimal separation, different peaks or patterns on the chromatogram correspond to different components of the separated mixture.
- A **chromatograph** is equipment that enables a sophisticated separation e.g. gas chromatographic or liquid chromatographic separation.
- The **eluate** is the mobile phase leaving the column.
- The **eluent** is the solvent that carries the analyte.
- The **retention time** is the characteristic time it takes for a particular analyte to pass through the system (from the column inlet to the detector) **under set conditions**.

The Chromatogram





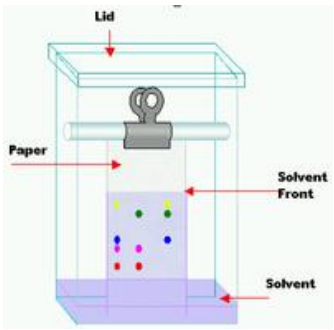
Plotted on the x-axis is the retention time and plotted on the y-axis a signal (for example obtained by a **spectrophotometer**, **mass spectrometer** or a **variety of other detectors**) corresponding to the response created by the analytes exiting the system. In the case of an optimal system the signal is proportional to the concentration of the specific analyte separated.

Idenitfying Components

Measure how far a component moves during chromatography and determine its "retention factor" (Rf value). The same substance will have the same Rf value on the same chromatogram (see Fig. 6.3 on p.63 of text).

$$R_f = \frac{\text{distance moved by the component form the origin}}{\text{distance moved by the solvent form the origin}}$$

The R_f value for any chemical will change if there is are changes in: temperature, the type of stationary phase, the type of solvent and the amount of water vapour around the plate or paper.



28 Experiment

Chromatography of inks and Smarties

Purpose

To separate the components of colourings used in inks and Smarties and to identify some of the colours used in Smarties.

Procedure

Part A—Chromatography of inks

1 Pour 1% sodium chloride solution into a 250 mL beaker to a depth of about 1 cm.
2 Using a pencil, draw a line about 2 cm from one narrow end of a sheet of chromatography paper. This line is known as the origin.
3 Apply up to five spots of ink at equal distances along this line using felt-tipped pens of different colours.
4 Straighten out a paperclip and thread it through the other narrow end of the paper so that the paper hangs in the beaker with the bottom of it just touching the liquid. Ensure the ink spots are not immersed.
5 Allow the liquid to rise up the paper to a height of about 7 cm.
6 Remove the strip of paper and immediately record the level the liquid has reached with a small pencil mark on the edge of the paper.

Part B—Identifying food colours in Smarties

1 Select a Smartie (black, brown, orange, green and violet Smarties give the most interesting results). Place the Smartie on a watch glass and add a drop or two of water to dissolve the food colour. (Use as little water as possible so that the solution formed is concentrated.)
2 Draw some of the food colour into a capillary by placing it in the solution. Touch the end of the capillary lightly and quickly on the origin of a sheet of chromatography paper so that a *small* spot forms. Allow the spot to dry and repeat the procedure to make a more concentrated spot.
3 Repeat this procedure using a Smartie of another colour and then using the standard food dyes that have been provided. Because the solutions of the standards are concentrated, apply only one drop on the origin. Run a chromatogram according to the procedure described in Part A.

Theory

Many dyes are composed of a mixture of different coloured components. These components can be separated by the technique of paper chromatography. The principles of chromatography are described in *Heinemann Chemistry 2*, Chapter 6.

Questions

1 Why do the components of the dyes separate as they move up the chromatography paper?
2 Why is the original site of the spots (the origin) marked with a pencil instead of a pen?
3 Why must the spots be above the level of the solvent at the beginning of the experiment?
4 Why do different solvents give different chromatograms?
5 Calculate the R_f value of each component and tabulate your results under the headings 'Sample', 'Solvent', 'Colours of components', and 'R_f values'.
6 Which dyes were present in the Smarties you tested?
7 Describe a use for chromatography in industry.

Duration

40 minutes

Materials

- 25 mL 1% sodium chloride solution
- water-soluble, felt-tipped pens
- Smarties
- solutions of standard food dyes: 102 tartrazine, 122 azorubine and 133 brilliant blue FCF
- 2 × paperclips
- 2 × 250 mL beakers
- 2 × sheets (6 cm × 12 cm) of chromatography paper
- 2 × watch glasses, small
- 5 × glass capillaries (melting point tubes)
- pencil and ruler

Safety

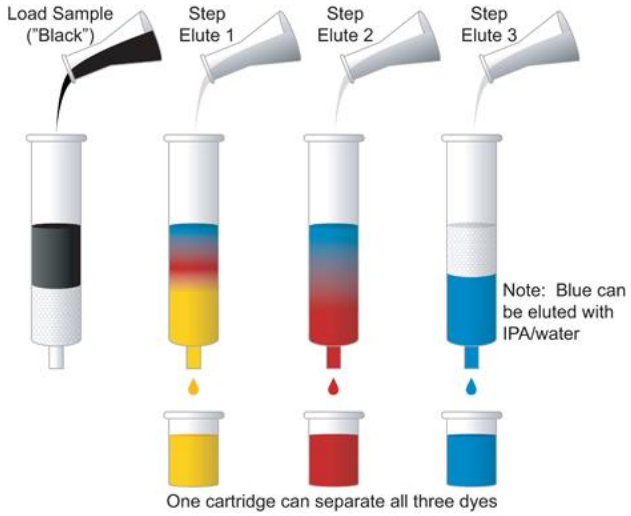
- The Smarties should not be eaten. Remember that substances used in the laboratory should not be tasted.

Chemical Analysis – Student Booklet

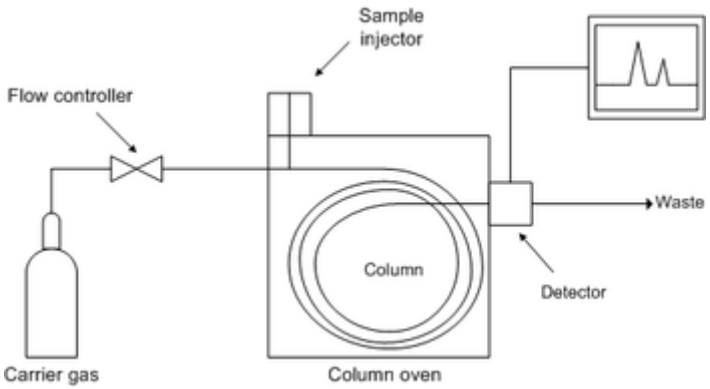
HPLC (High Performance Liquid Chromatography) & GLC (Gas, Liquid Chromatography)

Key Concepts

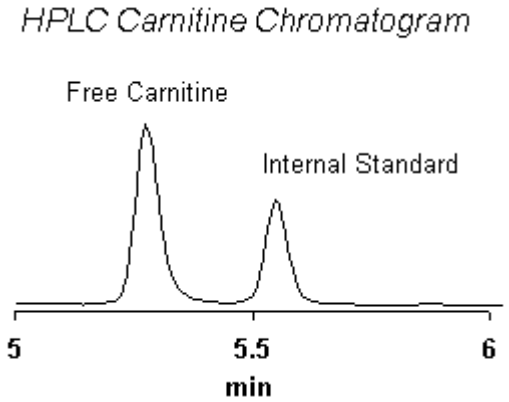
- Chromatography can be qualitative (identify the type of chemicals that are present in a mixture by comparing R_f and R_t values to experimental standards) and some forms of chromatography can be quantitative (tell you how much of each compound is present by measuring the area under peaks on chromatogram graphs for HPLC and GLC and then comparing these areas to the peak areas of standards with known concentrations that are run on the same chromatogram)
- Calibration Curves are graphs that measure concentration against absorbance or % area for chromatograms
- Factors that affect the R_t (Retention Time) include: temperature, the type of mobile phase, the type of stationary phase, the flow rate of the eluent or carrier gas, the pressure, the length of the chromatographn column etc.
- The rate at which a sample passes through the column is directly proportional to the temperature of the column. The higher the column temperature, the faster the sample moves through the column. However, the faster a sample moves through the column, the less it interacts with the stationary phase, and the less the analytes are separated.



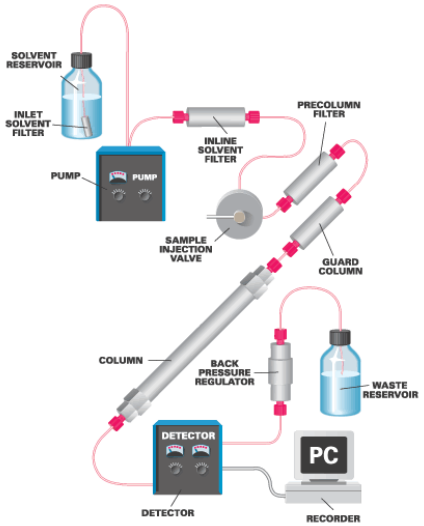
A **Column Chromatograph**. Gravity casues the sample to pass down the column. The eluate is collected over time in separate containers as pure sanmples of individual compounds.



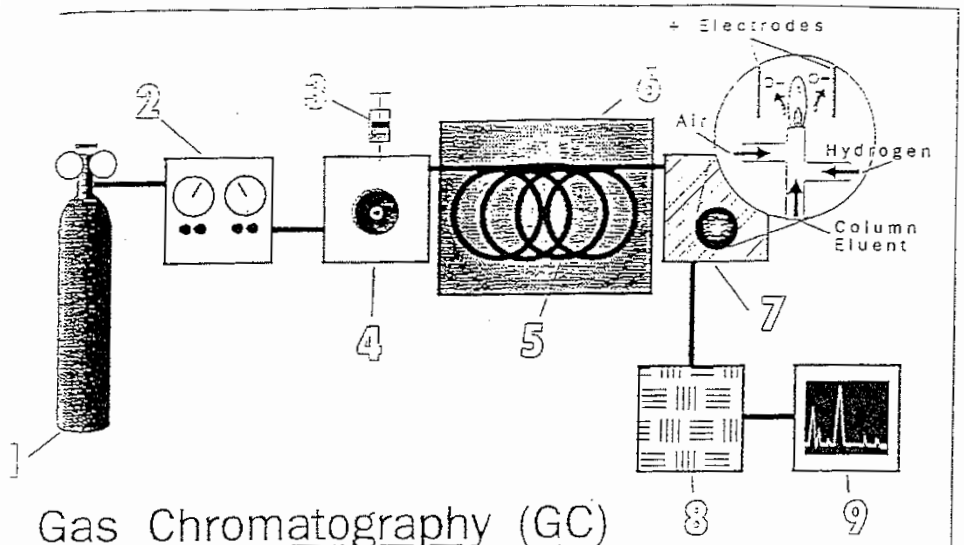
A **Gas Chromatograph**. The column is coiled to enable a very long column to be housed in a compact oven. A long column increases retention time and hence allows better separation of compounds.



An **internal standard** in analytical chemistry is a chemical substance that is added in a constant amount to samples, the analyte and calibration standards, in a chemical analysis. The internal standard is used for calibration by plotting the ratio of the analyte signal to the internal standard signal. This provides an accurate measure of the concentration of the analyte. This process is done to correct for the loss of analyte during sample preparation or sample injection. The internal standard is a compound that is very similar, but not identical, to the chemical species of interest in the samples.



A **HPLC Chromatograph**. A pump (rather than gravity) provides the higher pressure required to move the mobile phase and sample components through the densely packed column. The increased density arises from the use of smaller sorbent particles. Such particles are capable of providing better separation on columns of shorter length when compared to ordinary column chromatography.



Gas Chromatography (GC)

1 _____

2 _____

3 _____

4 _____

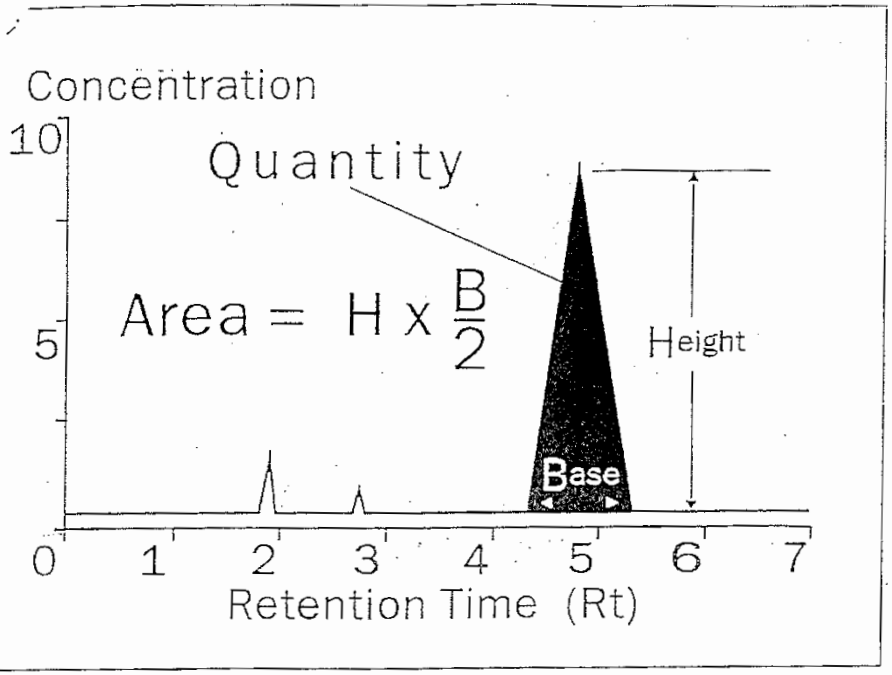
5 _____

6 _____

7 _____

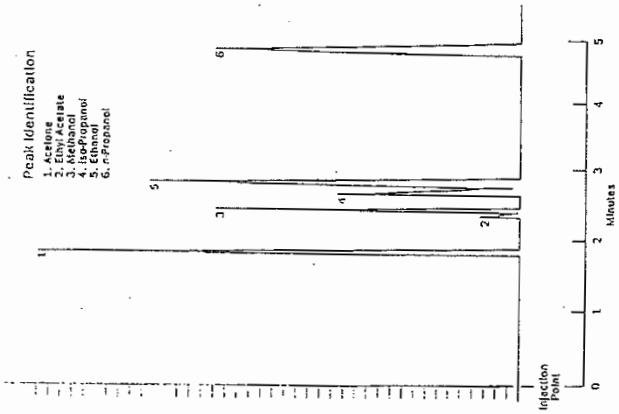
8 _____

9 _____



Chromatogram

Alcohol Chromatogram



Chromatography

To run any chromatograph you need 3 basic ingredients:

- an experimental sample which contains a mixture of compounds that you wish to separate
- an inert solvent (or inert gas carrier) to dissolve the experimental sample (the solvent and gas carrier must not chemically alter the experimental sample)
- a stationary material which has the capacity to retard the progress of any chemical which is passed over or through it

The mobile and stationary phases

- the mobile phase = the solvent
- the stationary phase = stationary material (usually a solid material which doesn't move)

To make sense of running a paper or thin layer chromatograph

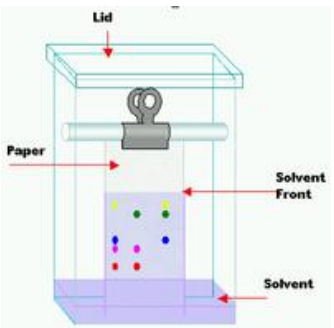
- you need to determine the R_f values of all components in the experimental sample
- you need the results from running controls against your unknowns eg. comparing the separation of amino acids from orange juice with a number of pure amino acid samples that are run as controls

Different types of chromatography

- paper chromatography, thin layer chromatography, column chromatography, high performance liquid chromatography and gas-liquid chromatography

Type of Chromatography	Stationary Phase	Mobile Phase	Types of samples that can be run	How are the results interpreted
paper chromatography	high quality adsorbant paper	a suitable inert solvent	samples in solution ie. mixtures of compounds which adsorb to differing degrees	R_f values
thin layer chromatography				

Retention factor: $$R_f = \frac{\text{distance moved by the component form the origin}}{\text{distance moved by the solvent form the origin}}$$



Chemical Analysis – Student Booklet

Type of Chromatography	Stationary Phase	Mobile Phase	Types of samples that can be run	How are the results interpreted
column chromatography				
high performance liquid chromatography				
gas-liquid chromatography				

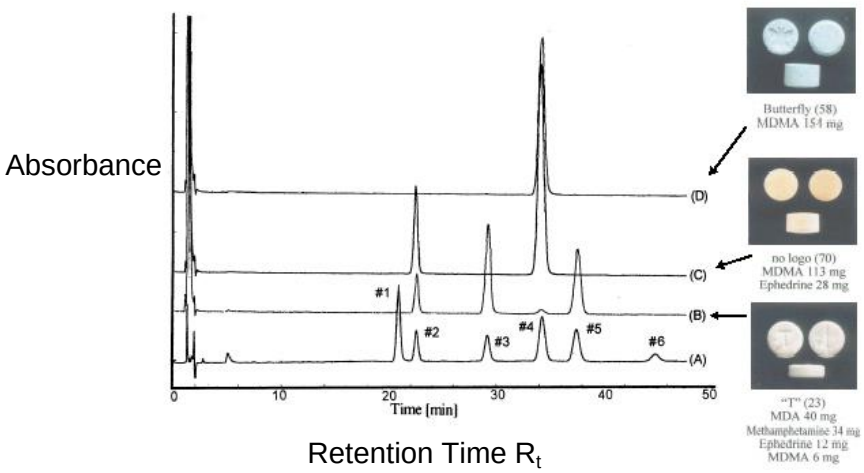
High Performance Liquid Chromatography

- pressure = 14,000 kPa ≅ 139 atmospheres
- absorbance: measured by a UV/visible spectrometer; *absorbance ∝ concentration*
- R_t = Retention Time = how long individual samples take to pass through the column
- can be used for large compounds (RMM ≥ 1000)

Example of a HPL chromatogram:

Gas-liquid Chromatography

- concentration: a *flame ionisation detector* ionises compounds as they leave the column of the GL machine, these ions produce an electrical current. The greater the current, the greater the number of ions produced: *concentration ∝ current*
- limited to samples that can be vaporised without decomposing (RMM < 300)
- very sensitive: capable of detecting 10^{-12} g of a compound

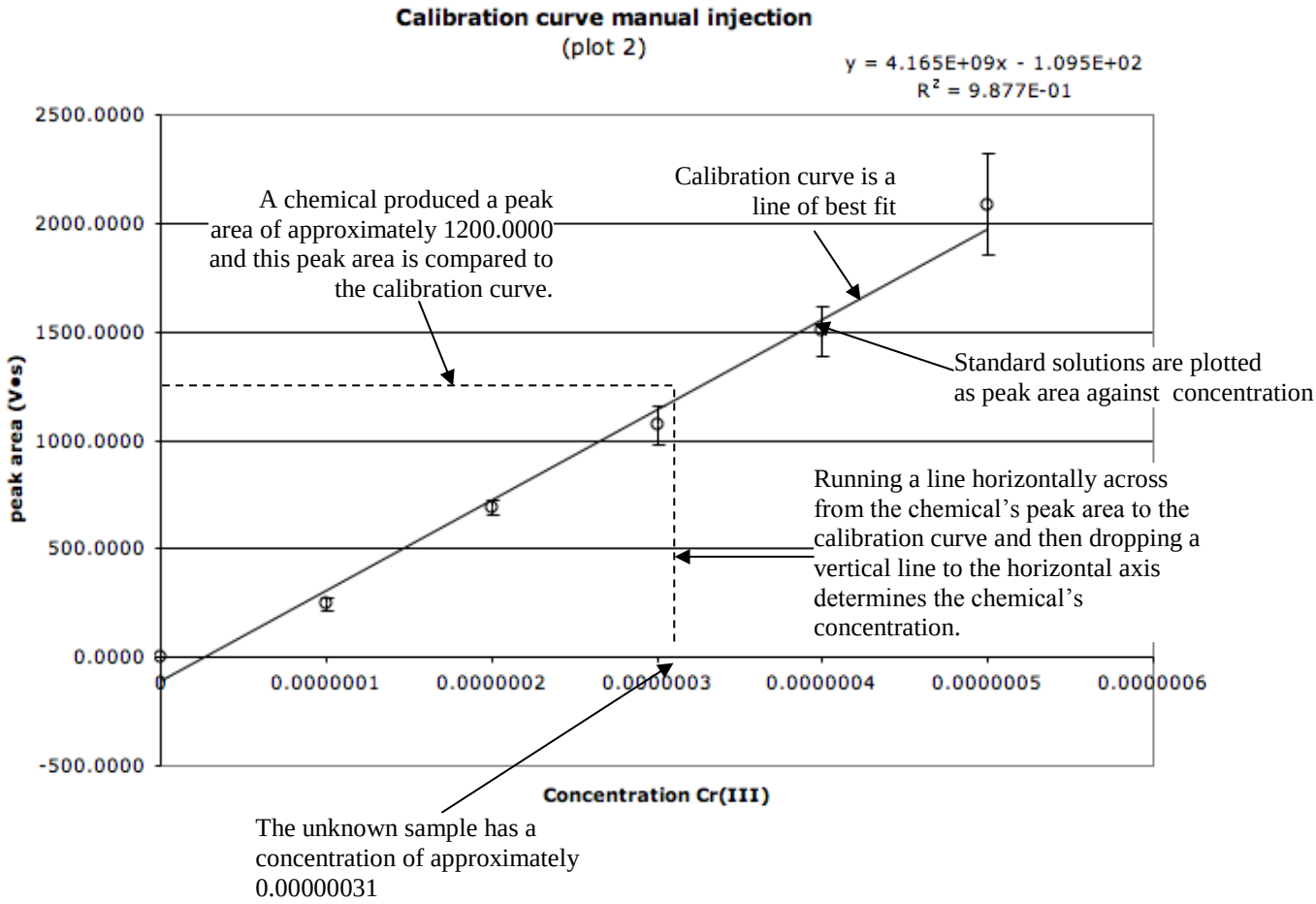


The area inside the peaks on a chromatogram is a measure of concentration.

Calibration Curves in Chromatography

The peak area that a chemical produces on a chromatogram can be used to determine the concentration of that chemical if a calibration curve has been produced. By using a series of samples with accurately known concentrations (standard solutions), and by plotting these concentrations against the peak areas produced by each of these samples, the concentration of unknown test samples can be determined.

Example: using the calibration curve of a number of Cr III Standard Solutions



30 Exercise

Ethanol content of wine by gas chromatography—data analysis

Purpose

To determine the percentage of ethanol in a sample of wine using data from gas chromatography.

Procedure

The ethanol content of a sample of wine in an old wine cask was found by preparing the following standards: 4.0%, 8.0%, 12.0% and 16.0% ethanol (Table 30.1).

Four mL, 8.0 mL, 12.0 mL and 16.0 mL ethanol was measured accurately by pipette and placed in separate 100 mL volumetric flasks. Twenty mL propanol was pipetted into each flask and then the volume made up to the 100 mL mark with distilled water.

Table 30.1 Uncertainty of results

Sample	Concentration of ethanol (%)	Percentage propanol
Standard 1	4.0	20
Standard 2	8.0	20
Standard 3	12.0	20
Standard 4	16.0	20
Sample	unknown	20

The wine sample was prepared by pipetting 50 mL of wine into a standard flask, adding 20.0 mL propanol and diluting it to 100 mL with distilled water.

Ten µL of each standard and the sample was injected onto the column of a gas chromatograph fitted with a flame ionisation detector.

Theory

The ethanol content of wine can be determined quickly, reliably and accurately by gas–liquid chromatography. For quantitative analysis, the peak area of the ethanol in the wine sample can be compared to the peak areas of known concentrations of ethanol standards, run under identical conditions.

One of the greatest sources of error in the analysis lies in the injection of the samples onto the column. A syringe is used to inject samples as small as 0.1 µL onto the column. Significant errors can arise because of very small differences in the tiny sample size. This problem can be overcome by the use of an internal standard. An internal standard is a compound similar to the one under investigation. The same known amount is added to the sample and standards alike.

Propanol is used as the internal standard for ethanol. Any change to the ethanol peak due to loss of the sample during injection will occur to the same extent to the propanol peak. These errors can be compensated for by measuring the ratio of the ethanol peak to the propanol peak rather than the ethanol peak alone.

The boiling points of ethanol and propanol are, respectively, 78°C and 97°C. The theory and principles involved in gas chromatography are described in *Heinemann Chemistry 2*, Chapter 6.

Results

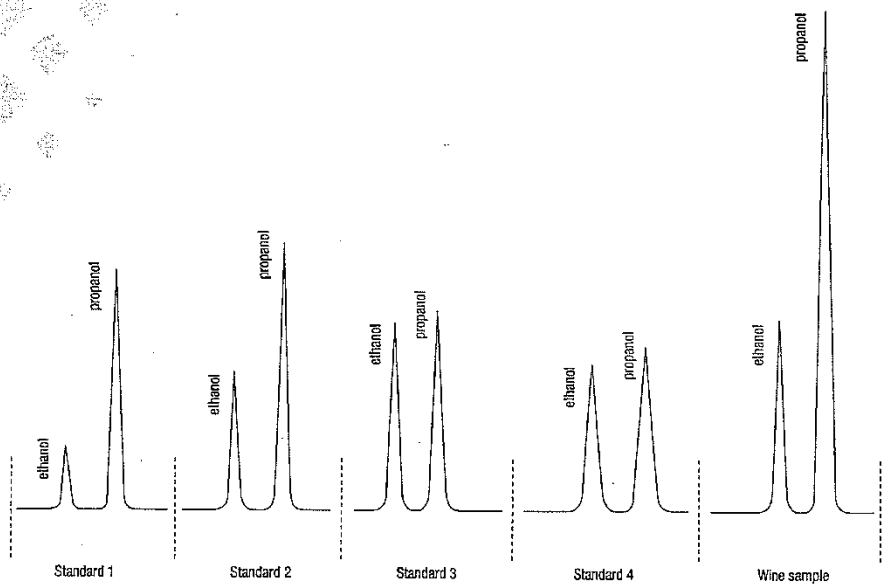


Figure 30.1 Chromatograms obtained from each sample

The peak areas of the ethanol peak and the propanol peak for each standard and sample was measured by the integrator in the gas chromatography. The results are shown in Table 30.2.

Table 30.2 Peak areas of ethanol and propanol

Sample	Peak area of ethanol	Peak area of propanol
Standard 1	418 530	1 561 900
Standard 2	868 420	1 662 200
Standard 3	942 460	1 144 700
Standard 4	1 252 000	1 259 600
Diluted wine	1 007 780	3 010 600

Questions

1 Suggest why the ethanol peak occurs before the peak for propanol in each chromatogram.

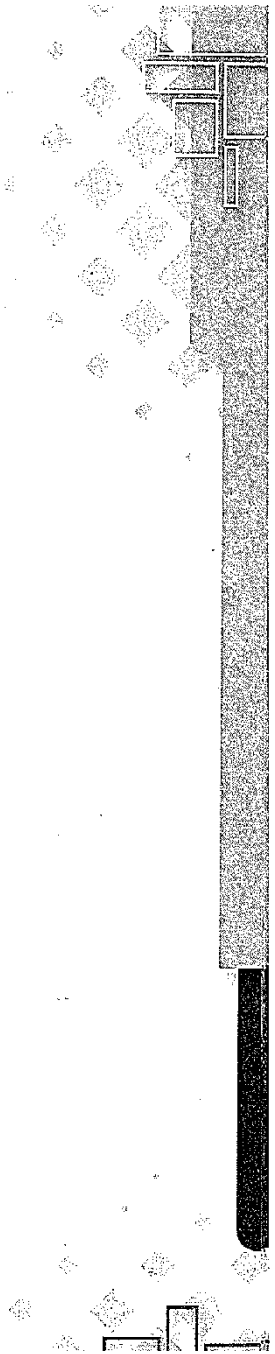
2 In practice the chromatograms were obtained at a temperature of 110°C. Why would a temperature of 60°C be unsuitable?

3 Complete Table 30.3.

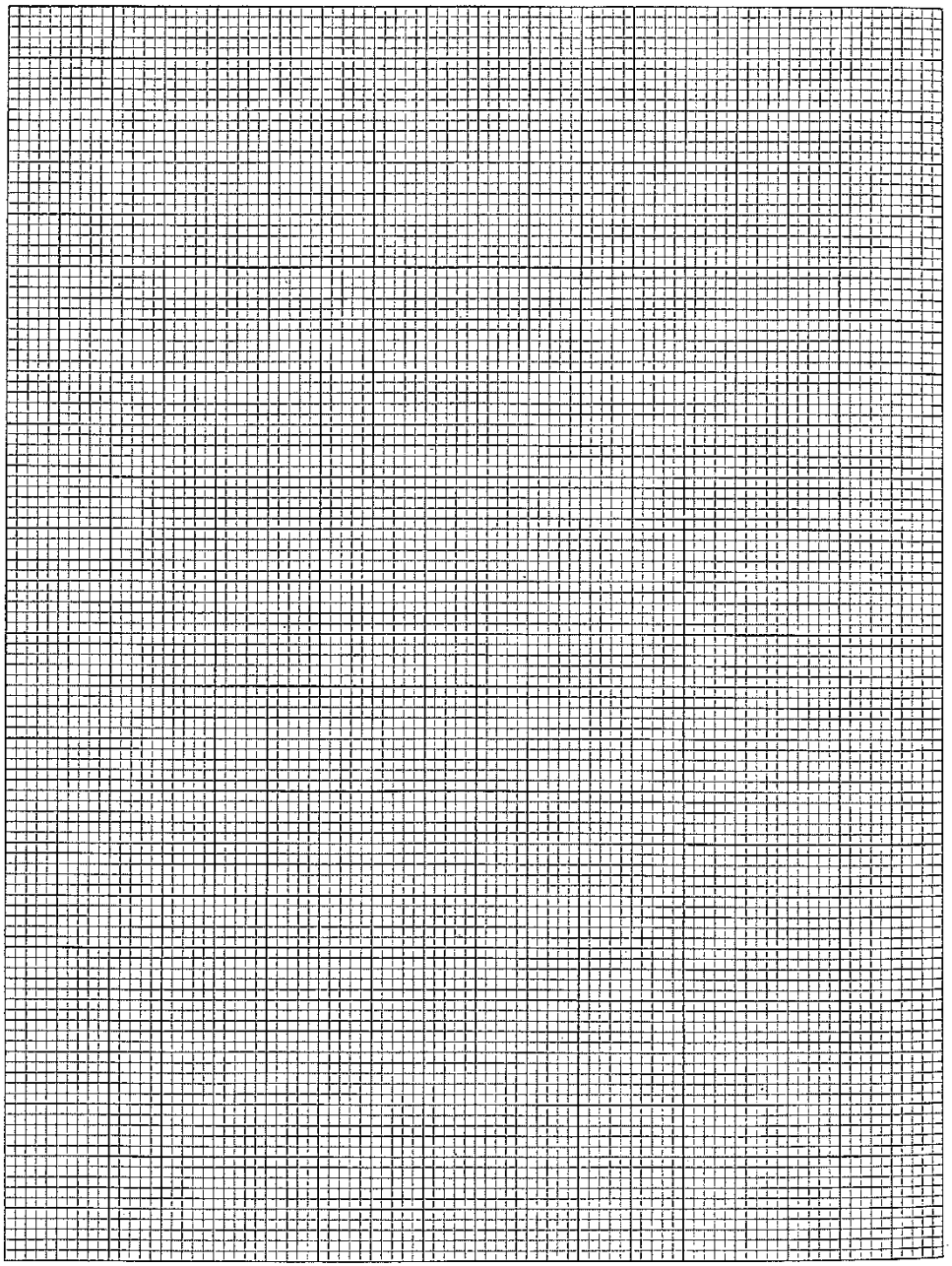
Table 30.3 Uncertainty of results

Sample	Concentration of ethanol (%)	Ratio of peak areas ethanol:propanol
Standard 1		
Standard 2		
Standard 3		
Standard 4		
Diluted wine	unknown	

4 Plot a calibration graph with the concentration of ethanol on the *X*-axis and the ratio peak area of ethanol:peak area of propanol on the *Y*-axis. The graph passes through the origin.
5 Use the graph to find the percentage concentration of ethanol in the diluted wine sample.
6 Calculate the percentage concentration of ethanol in the original wine.
7 The label on the cask of wine stated that the ethanol content was 11.5%. Give a possible explanation for the difference between the experimental value and the stated value (other than a simple mistake in performing the analysis).
8 Sketch and label a diagram showing the main components of a gas chromatograph.
9 Briefly describe the chemical principles that form the basis of the operation of the instrument.



2 millimeters/Division 5th Accent



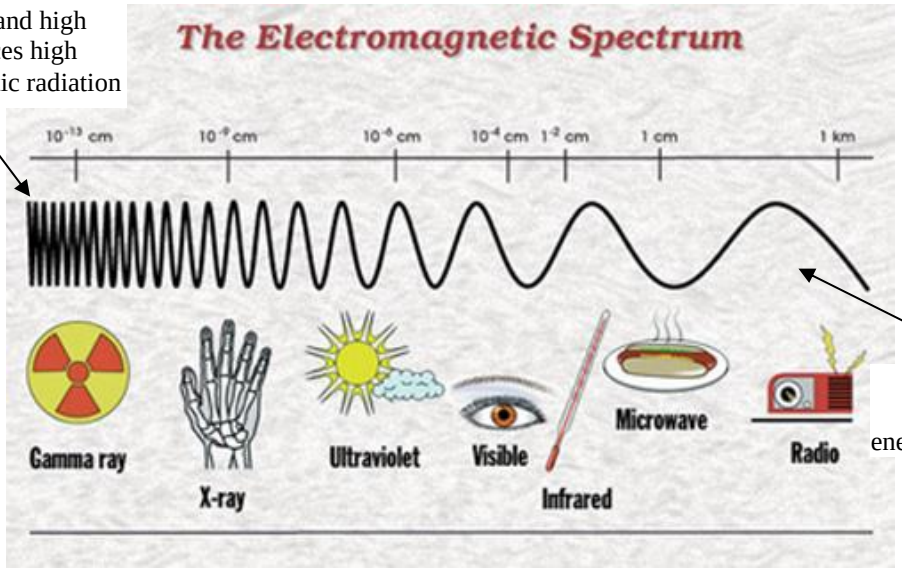
Spectroscopy – Text Ref pp.77-80

Spectroscopy is the study of how electromagnetic radiation interacts with matter (atoms and molecules). The nature of these interactions depends upon the energy of the electromagnetic radiation. What is electromagnetic radiation? **Electromagnetic radiation** (**EM radiation** or **EMR**) is a form of energy emitted and absorbed by charged particles, which exhibits wave-like behavior as it travels through space. EMR has both electric and magnetic field components.

Electromagnetic radiation interacts with material continually. One good example is an object being heated when left in sunlight. The object absorbs energy in the form of electromagnetic radiation and heats up. A critical concept in the interaction of matter and electromagnetic radiation is that the energy absorbed is always released. When a hot object is placed in the shade it releases energy and cools down.

Spectroscopy is the study of how electromagnetic radiation interacts with matter (atoms and molecules). The nature of these interactions depends upon the energy of the electromagnetic radiation and the quantum, or energy levels, within atoms. As electromagnetic radiation is absorbed by an atom, electrons are promoted to higher energy levels and the atom is said to be excited. A single electron excitation requires a single quantum of energy (a photon) that exactly matches the energy required for an electron to jump between 2 energy levels (electron shells). The atoms of all elements have unique electron shell configurations and therefore require unique photons to become excited. Following excitation, electrons return to their ground state releasing the energy absorbed.

short wavelength and high frequency produces high energy electromagnetic radiation



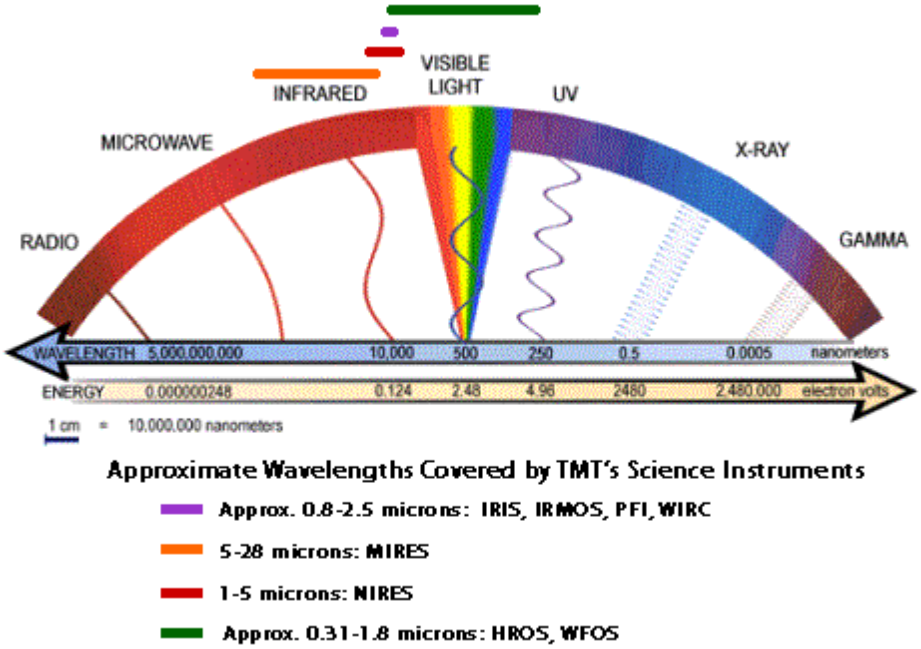
long wavelength and low frequency produces low energy electromagnetic radiation

Refer to p.77 of the text and list the 3 piecs of information that spectroscopy can provide about a chemical under analsysis.

-
-
-

List the 3 points on p.77 which explain how spectroscopy works.

-
-
-



Complete Table 7.1 on p.78

Spectroscopic Technique	Part of the electromagnetic spectrum	Wavelength range (cm)	Part of atom or molecule affected
Ultraviolet Spectroscopy (UV)			
Colorimetry			
Atomic Absorption Spectroscopy (AAS) & Atomic Emmision Spectroscopy (AES); Flame Tests			
Infrared Spectrscopy (IR)			
Nuclear Magnetic Resonance Spectroscopy (NMR)			

Flame Tests – text ref pp.78-80

A crude qualitative test that is used as a guide to identify some metal ions based on the colour of light that they emit when heated in a Bunsen flame. When metals ions are heated in a flame electrons are excited into a higher electron shell. These electrons return to the ground state within a split second and release energy of a typical colour. **REFER TO FIG 7.7 ON P.79 OF TEXT – WRITE THIS DOWN**

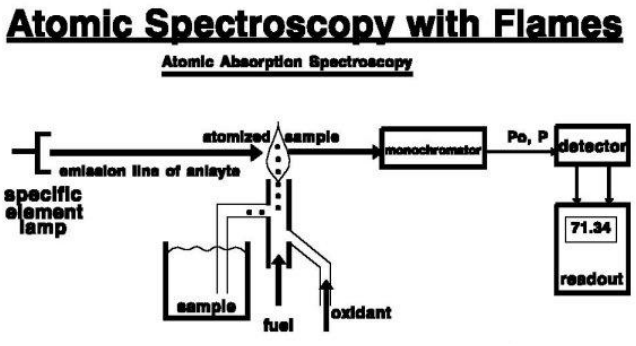
Practical Flame Testing

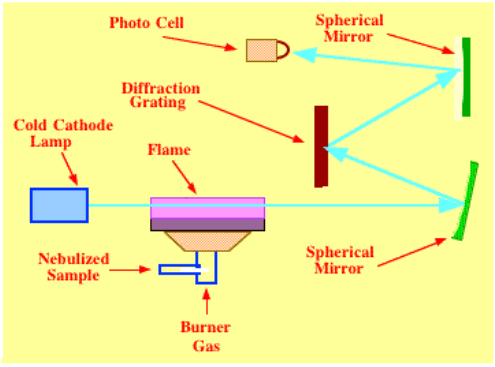
Compound	Metal Cation	Flame Colour

Colorimetry, Calibration Curves & the Atomic Absorption Spectrometer

Key Concepts

- Atoms, molecules and subatomic particles interact with (absorb and emit) electromagnetic radiation of specific energies known as **quanta**.
- Flame Tests, Colourimetry, Atomic Emission Spectroscopy, Atomic Absorption Spectroscopy and UV-Visible Spectrocopy are all techniques based upon the excitation of electrons by electromagnetic radiation of various quanta
- When atoms absorb quanta using these techniques electrons are promoted from their "ground state" (their lowest and most stable energy state) to an "excited state" (an abnormally high energy state that is unstable)
- Excited electrons naturally return to their ground state and emit the energy that they absorbed
- The total energy absorbed = total energy released, **but the quanta (photons) may be of different sizes**
- The amount of energy in a quanta can be calculated using the equation: $E = \frac{hc}{\lambda}$ where λ = the wavelength of light, and h and c are constants
- Put more simply: $E \propto \frac{1}{\lambda}$ ie. light with small wavelengths is high energy
- Colorimetry is an analytical technique that determines the concentrations of solutions by measuring how much light a solution absorbs ie. higher concentration implies more atoms present to absorb light
- Calibration Curves can be created practically by using a colorimeter





Calibration Curves in techniques that rely on the excitation of electrons

In any experimental sample, the more atoms or molecules present in a sample the more of a specific wavelength of electromagnetic radiation will be absorbed. By using a series of samples with accurately known concentrations, many forms of spectroscopy can determine the concentration of unknown test samples through the use of calibration curves.

Calibration Comment : Determining the concentration of CuSO4 solutions

Date : 2/03/2006 12:13 pm

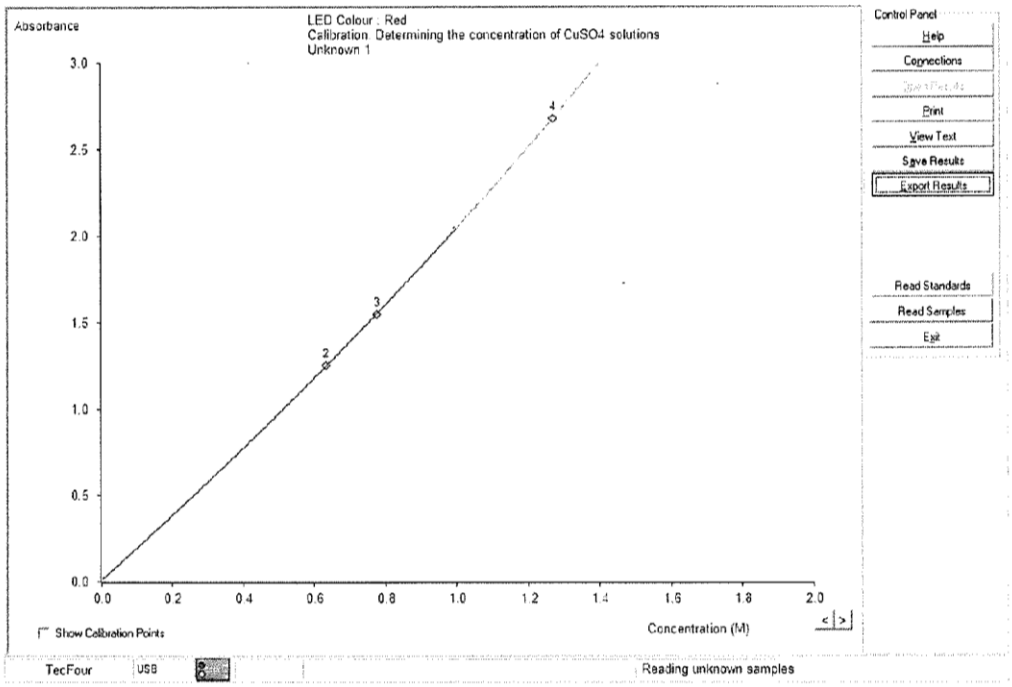
Concentration Unit : M
LED Colour : Red

Calibration Standards

No.	Concentration		Absorbance
1	0	M	0.00
2	0.2	M	0.42
3	0.4	M	0.77
4	0.6	M	1.32
5	0.8	M	1.45
6	1.0	M	2.08

Comment : Unknown 1
Unknown samples measured : 4

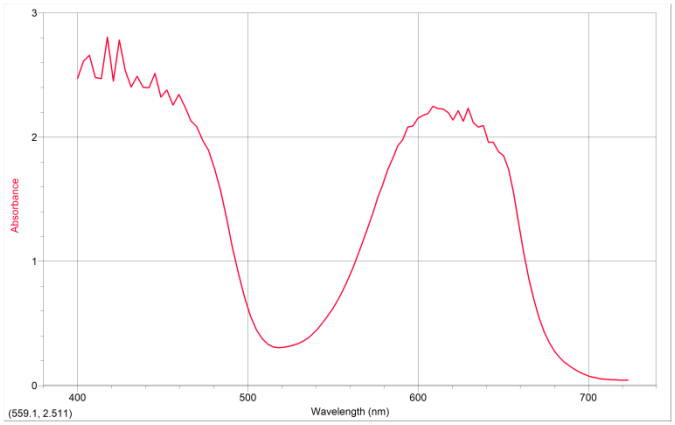
No.	Concentration		Absorbance	Comment
1	0.629	M	1.25	Sample No. 1
2	0.629	M	1.25	Unknwon 2
3	0.771	M	1.55	Unknown 3
4	1.266	M	2.68	Unknown 3



Chemical Analysis – Student Booklet

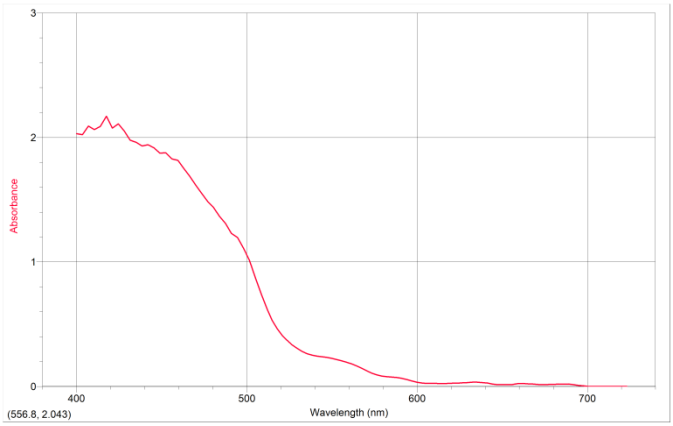
Absorbance Scanning to Determine the Most Suitable Wavelength for Spectroscopic Analysis

Green Food Dye



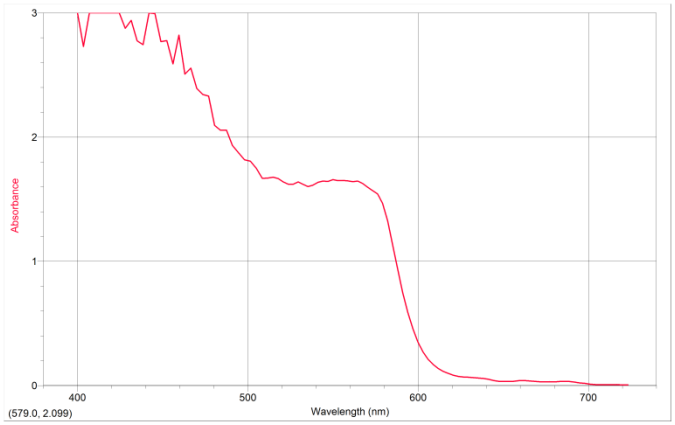
Most Suitable Wavelength: _____ nm

Yellow Food Dye



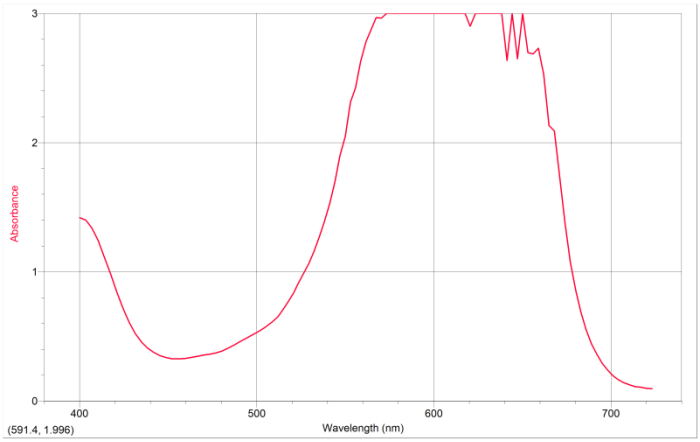
Most Suitable Wavelength: _____ nm

Red Food Dye



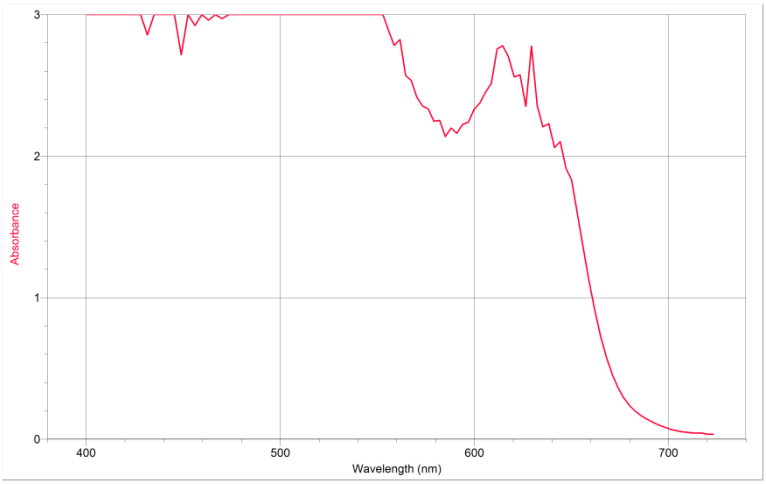
Most Suitable Wavelength: _____ nm

Blue Food Dye



Most Suitable Wavelength: _____ nm

Black Food Dye



Most Suitable Wavelength: _____ nm

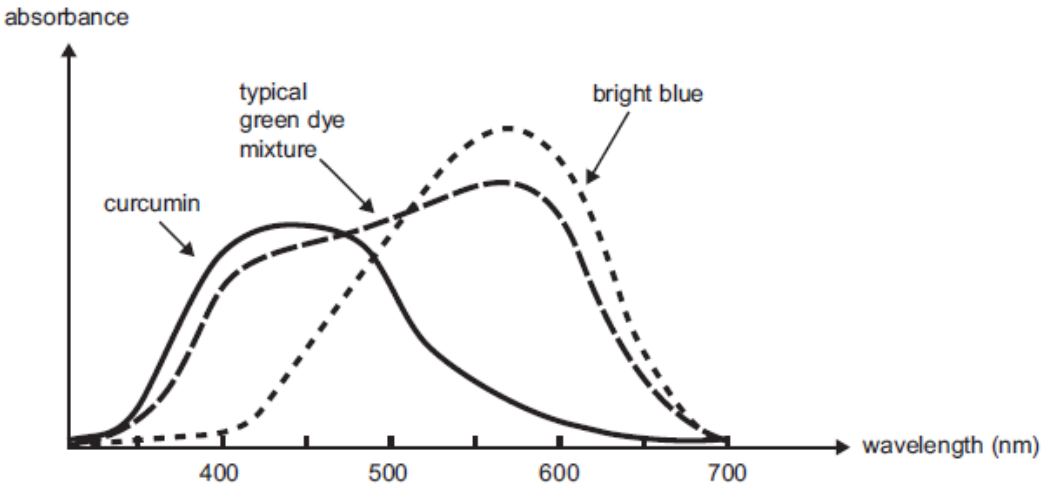
What wavelength would you select to detect the presence, and quantity, of Red Dye if it was in a mixture with Yellow Dye? Explain.

_____

VCAA – Exam 1 Spectroscopy Question (2006)

Question 4

A green dye used to colour tinned peas is made by mixing the yellow chemical, curcumin, with another colouring agent called bright blue. The individual spectra of curcumin, bright blue and a typical green dye are represented below.



UV-visible spectroscopy is used to analyse the curcumin content of tinned peas.

a. Circle the wavelength below which would be best used for absorbance measurements to determine the curcumin content of the peas.

400 nm 450 nm 500 nm 550 nm 600 nm 650 nm

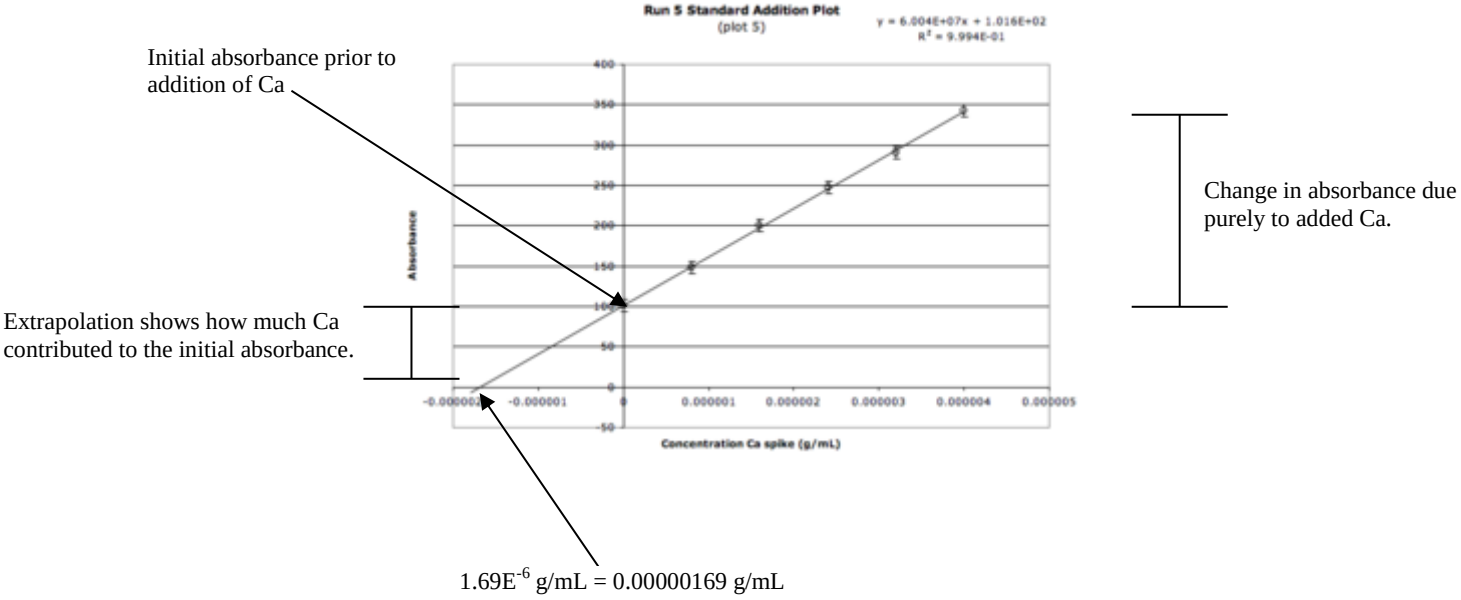
1 mark

At first glance you would expect that the most appropriate response to this question is 450 nm. However, you will notice that "bright blue" absorbs fairly strongly at 450 nm. Absorbance measurements taken at 450 nm would therefore be due to both dyes. At 400 nm "curcumin" still absorbs strongly where as bright blue does not – readings taken at 400 nm would therefore not be as prone to interference from "bright blue". In this instance, analysis should be undertaken at 400 nm.

On many occasions consumer products that undergo spectroscopic analysis contain more than one chemical that will absorb light of a particular wavelength. If there is no alternative other than taking measurements at a wavelength where more than one chemical absorbs a technique known as **Standard Addition** can be used.

Standard Addition

The method of **standard addition** is used in instrumental analysis to determine concentration of a substance (analyte) in an unknown sample by comparison to a set of samples of known concentration, similar to using a calibration curve. Standard addition can be applied to most analytical techniques and is used instead of a calibration curve to solve the problem of other chemical species absorbing light at the selected wavelength and therefore compromising the final result – this is known as the *matrix effect*.



Example standard addition plot.

This graph is an example of a standard addition plot used to determine the concentration of calcium in an unknown sample by atomic absorption spectroscopy. The point at zero concentration added Ca is the reading of the unknown, the other points are the readings after adding increasing amounts ('spikes') of standard solution. The *absolute value of the x-intercept* is the concentration of Ca in the unknown, in this case $1.69E^{-6}$ g/mL.

Standard addition is frequently used in atomic absorption spectroscopy and Gas Chromatography. The matrix effect problem occurs when the unknown sample contains many impurities. If impurities present in the unknown interact with the analyte to change the instrumental response or themselves produce an instrumental response, then a calibration curve based on pure analyte samples will give an incorrect determination.

One way to solve this problem is to use standard addition. The standard solution (solution of known concentration of analyte) is added to the unknown solution so any impurities in the unknown are accounted for in the calibration. The operator does not know how much was in the solution initially but does know how much standard solution was added, and knows how the readings changed before and after adding the standard solution. Thus, the operator can *extrapolate* and determine the concentration initially in the unknown solution. In practice, the volume of standard solution added is kept small to avoid dilution of the unknown impurities.

Atomic absorption spectroscopy (AAS)

In short, AAS works on the principle that the electrons of the atoms passed into the *atomizer* can be promoted to higher orbitals (excited state) for a short period of time (nanoseconds) by absorbing a defined quantity of energy (radiation of a given wavelength). This amount of energy, i.e. wavelength, is specific to a particular electron transition in a particular element. In general, each wavelength corresponds to only one element, and the width of an absorption line is only of the order of a few picometers (pm); this gives the technique its elemental selectivity.

The design feature that gives an AAS its elemental specificity to test for a single metal is the hollow *cathode ray lamp*. This lamp is constructed out of the metal that is under investigation. For example, an analysis to determine the concentration of copper in a sample will employ the use of a cathode ray lamp constructed from copper. When an electrical current passes into the cathode ray lamp, the atoms in the element of the lamp will become excited and then emit photons of emr unique to that metal. This means that only copper atoms in the sample will absorb light emitted from the lamp because the light will contain photons that are unique to the energy levels within copper atoms.

Each element will preferentially absorb light at a particular wavelength, due to each element having a defined and discrete quantity of energy required to promote its electrons into higher orbitals (excited state). During atomic absorption testing, a known amount of energy is passed through an atomized sample, and by then measuring the quantity of light remaining after absorption it is possible to determine the concentration of the element being measured.

The concentrations of metals under investigation are determined by applying the *Beer-Lambert* rule which is essentially a comparison of the intensity of light shining into a sample compared to the intensity of the light after it has passed through the sample ie. a measure of absorption.

In any experimental sample, the more atoms or molecules present in a sample the more of a specific wavelength of electromagnetic radiation will be absorbed. By using a series of samples with accurately known concentrations, many forms of spectroscopy can determine the concentration of unknown test samples through the use of calibration curves.

34 Exercise

Concentration of caffeine in a cola drink by UV–visible spectroscopy—data analysis

Purpose

To determine the concentration of caffeine in a cola drink using data from UV–visible spectroscopy.

Procedure

1 Cola drink is poured into four 100 mL volumetric flasks.
2 Standard 1 is prepared as follows:
   a 5.0 mg of caffeine is weighed accurately and added to the first volumetric flask.
   b The flask is shaken to dissolve the caffeine and more cola is added to bring the liquid to the 100 mL mark.
3 Standards 2 and 3 are prepared in the same manner but using 10.0 mg caffeine and 15.0 mg caffeine respectively.
   The sample is cola with no additional caffeine added.
   The cola sample and standards are analysed using a UV–visible spectrophotometer set at a wavelength of 275 nm.

Theory

Caffeine found in tea, coffee and cola drinks absorbs ultraviolet light readily and so can be analysed by UV–visible spectrophotometry.

The label on a bottle of cola drink listed the following ingredients: carbonated water, sugar, caramel, phosphoric acid, flavours and caffeine.

The caramel and flavours also absorb ultraviolet light and so could interfere with the analysis. To avoid the problem with interferences, the caffeine is analysed using a technique called standard addition. The cola drink itself is used to prepare the standards. Differing amounts of pure caffeine are added to identical portions of the sample.

Questions

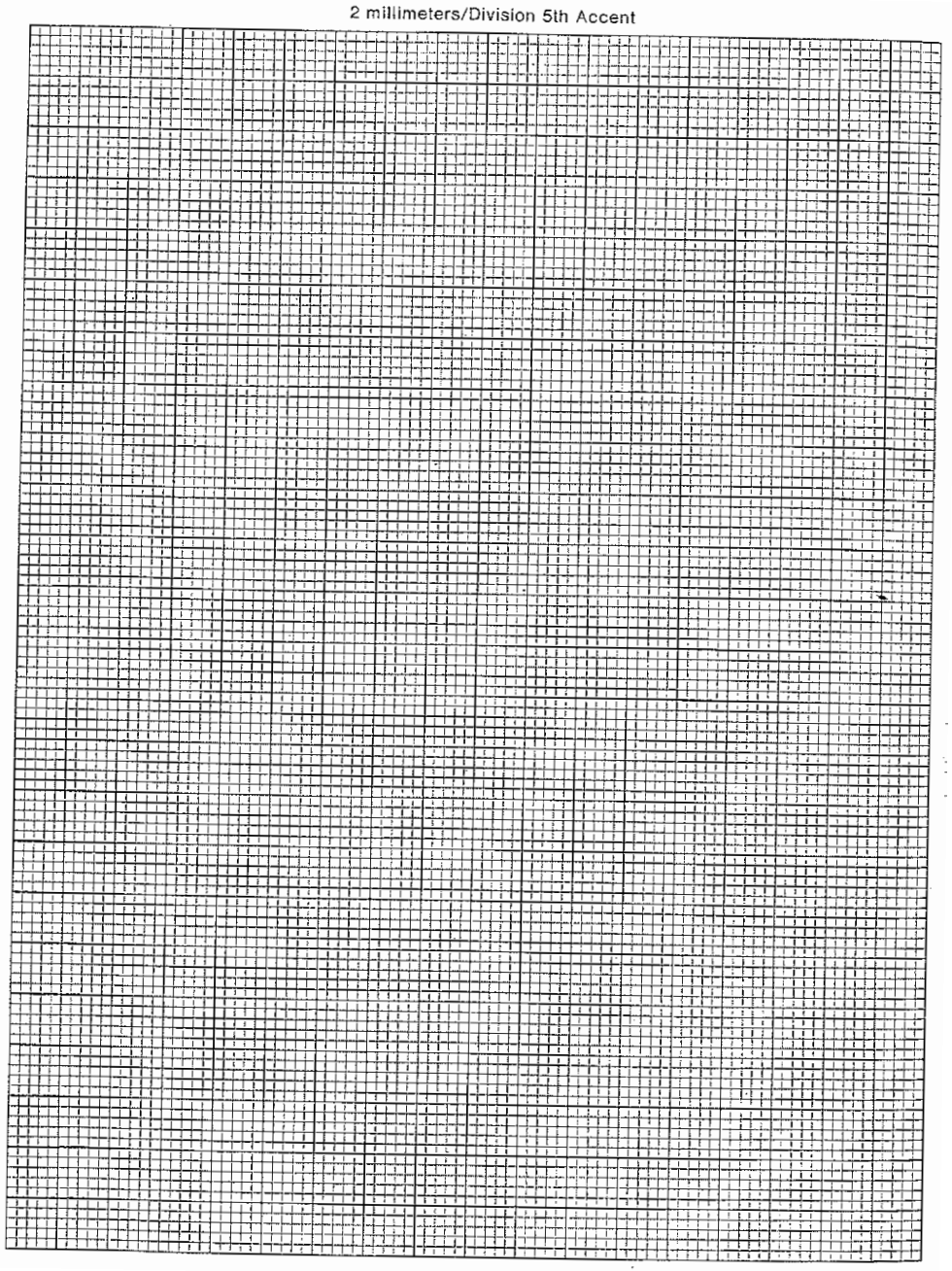
Use Table 34.1 to answer these questions.

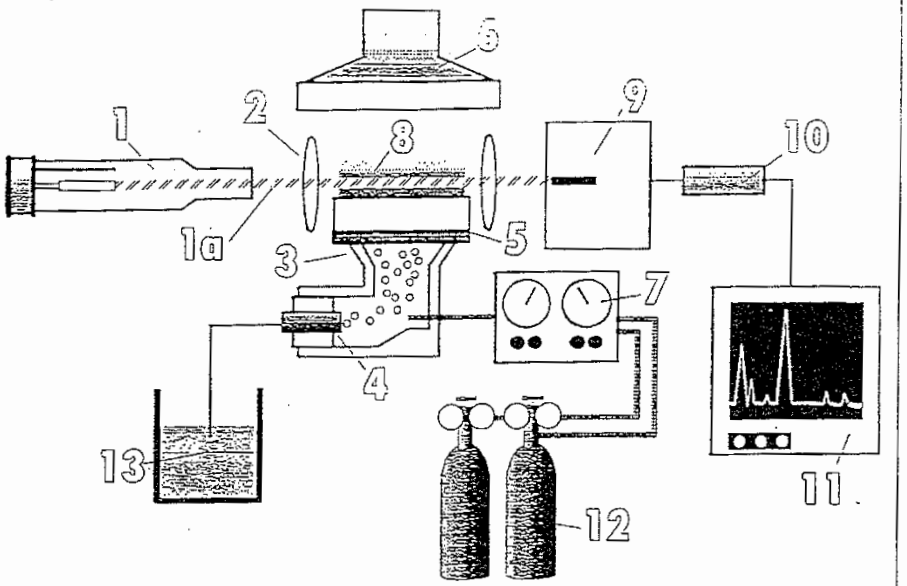
1 What does the term 'm' represent?
2 Plot a calibration curve of absorbance against mass, in mg, of caffeine added.
3 Draw a line of best fit through the points and extrapolate backwards to determine the intercept with the *X*-axis.
4 What mass of caffeine is present in 100 mL of this cola drink?
5 A single dose of 300 mg of caffeine can cause insomnia, restlessness, anxiety, palpitations, disturbances of vision and headaches. Would drinking a 1.25 L bottle of this cola drink be likely to cause these symptoms? Show your reasoning.
6 The molar mass of caffeine is 194 g mol^{-1}. Calculate the molarity of the caffeine in the cola drink.
7 Why would the wavelength of 275 nm have been chosen?
8 Sketch and label a diagram showing the main components of a UV–visible spectrophotometer.
9 Briefly describe the chemical principles that form the basis of the operation of the instrument.

Results

Table 34.1 Uncertainty of results

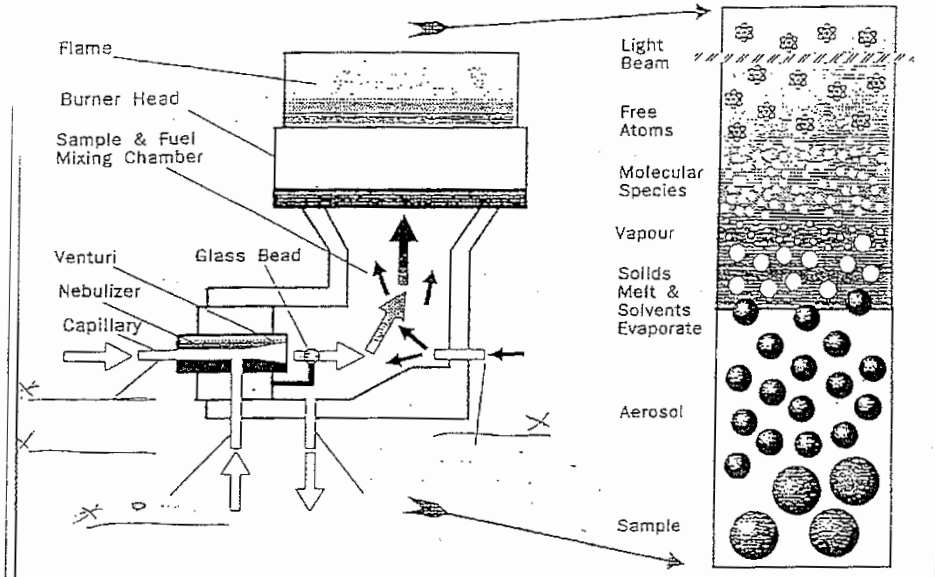
Standard	Mass of caffeine (mg)	Absorbance
Pure cola	m	0.250
1	m + 5.0	0.405
2	m + 10.0	0.560
3	m + 15.0	0.720



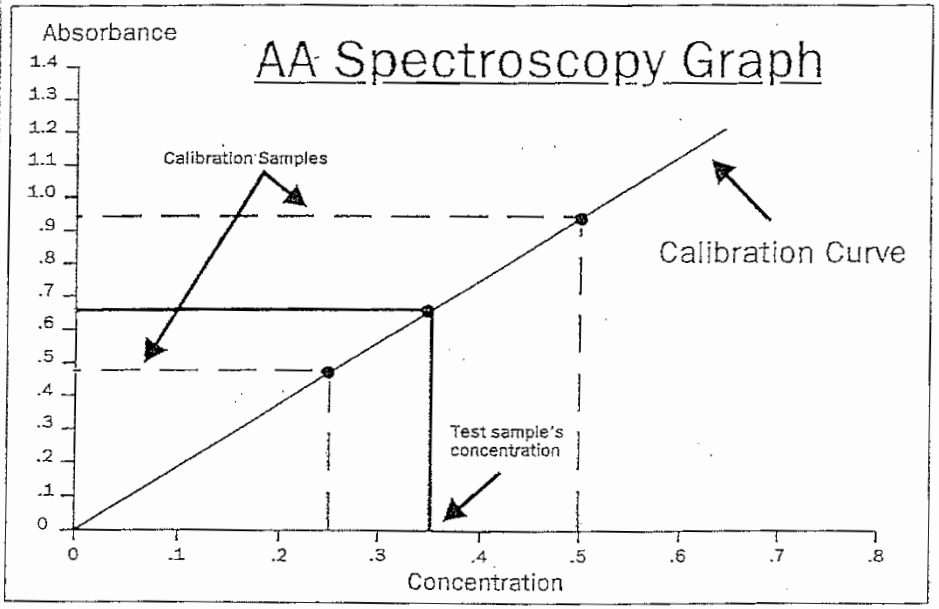


Atomic Absorption Spectrometer

1 _____
1a _____
2 _____
3 _____
4 _____
5 _____
6 _____
7 _____
8 _____
9 _____
10 _____
11 _____
12 _____
13 _____



Nebulizer & Burner Head



33 Exercise

Determination of concentration of iron in a breakfast cereal by atomic absorption spectroscopy—data analysis

Purpose

To calculate the concentration of iron in a sample of breakfast cereal using data from atomic absorption spectroscopy.

Procedure

The iron in a sample of breakfast cereal was determined using this technique. A 10.0 g sample of cereal was burnt to ash in a covered crucible. The ashes were dissolved in concentrated nitric acid and diluted to 100 mL with water.

A sample of the solution was injected into the flame of an atomic absorption spectrophotometer. The wavelength was adjusted to measure the light absorbed at 248.3 nm. A series of standards containing various concentrations of iron was also analysed. The results are shown in Table 33.1.

Theory

Iron is an essential component of the haemoglobin in our blood. Pregnant and menstruating women can have insufficient iron in their diets and so become anaemic. On the other hand, a high intake of iron can be dangerous for people who do not excrete excess iron readily. For both groups of people it is important to have information about the amount of iron in foods and medicines. The concentration of iron can be measured quickly, reliably and accurately by atomic absorption spectrometry. The theory and principles involved in the use of AAS are described in *Heinemann Chemistry 2*, Chapter 7.

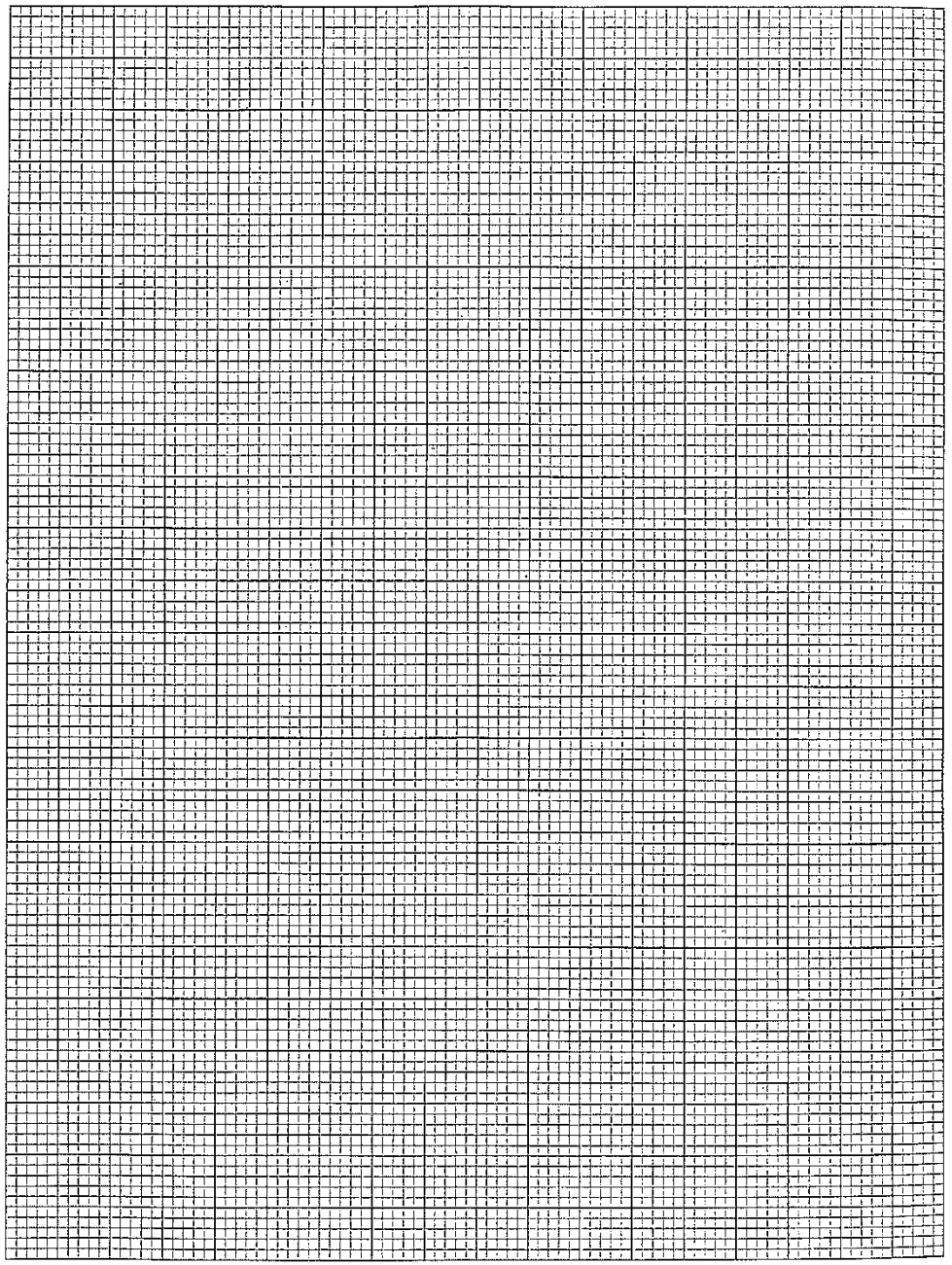
Results

Table 33.1 Results

Sample	Concentration of iron $\mu g\ mL^{-1}$ ($1\ \mu g = 10^{-6}\ g$)	Absorbance
Cereal solution	unknown	0.410
Standard 1	0	0.030
Standard 2	2.5	0.158
Standard 3	5.0	0.342
Standard 4	7.5	0.451
Standard 5	10.0	0.595

Questions

1 Plot a calibration graph of absorbance against concentration of iron from the data in Table 33.1.
2 What could account for the small reading in the 'zero' Standard 1?
3 What was the concentration of iron, in $\mu g\ mL^{-1}$, in the cereal solution?
4 What mass of iron was present in the ashes of the 10.0 g of cereal?
5 What is the concentration of iron, in mg per 100 g, in the cereal?
6 If the mass of iron in 100 g calculated in Question 5 represents 56% of the recommended daily intake (RDI) of iron, what is the RDI in mg?
7 What mass of this cereal would you have to eat to obtain your RDI of iron?
8 Why would the wavelength of 248.3 nm have been chosen?
9 Sketch and label a diagram showing the main components of an atomic absorption spectrophotometer.
10 Briefly describe the chemical principles that form the basis of the operation of the instrument.

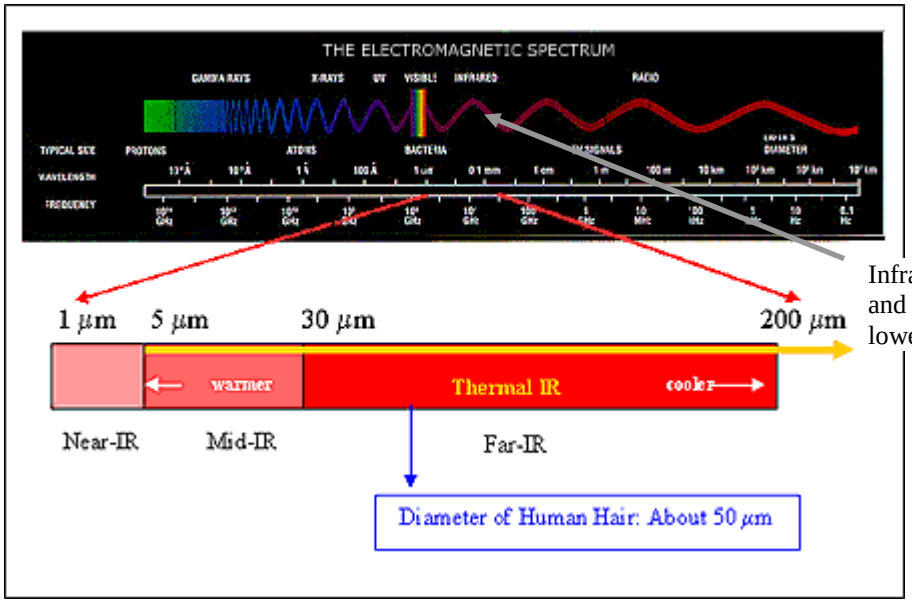


Chemical Analysis – Student Booklet

Infrared Spectroscopy – Text pp.89-95

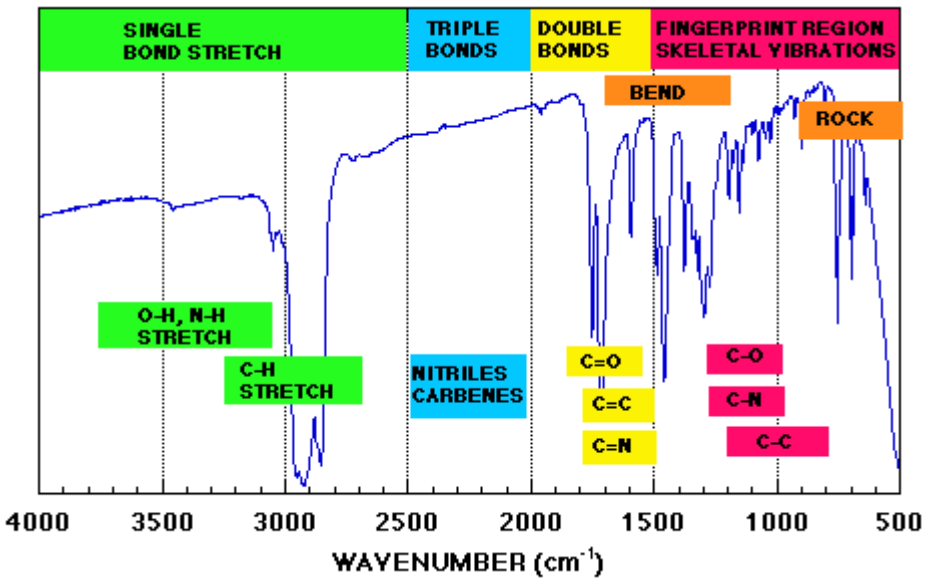
Electromagnetic radiation from the infrared region is of lower energy than UV and visble light.

High **Low Energy**

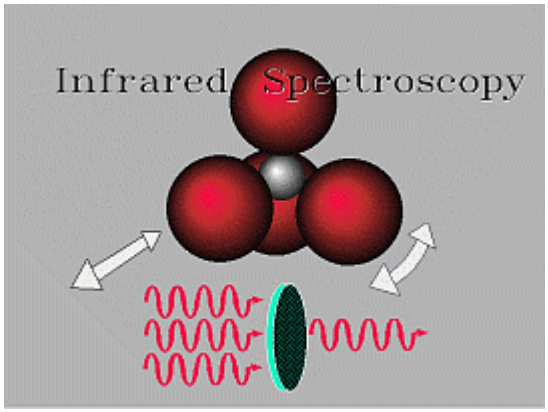


Infrared waves have long wavelengths and low frequency – they therefore are lower energy waves.

The lower energy infrared waves are not strong enough to cause electron excitation but they can cause changes in the bonds within molecules.



Different types of bonds absorb different energies (and therefore wavelengths) of infrared. To absorb infrared a molecule must have a **dipole moment** which means that there must be a polar bond present in a molecule which will produce a separation in charge caused by the unequal sharing of electrons.



There is one common type of molecule that does not have a dipole moment. What is it?

_____

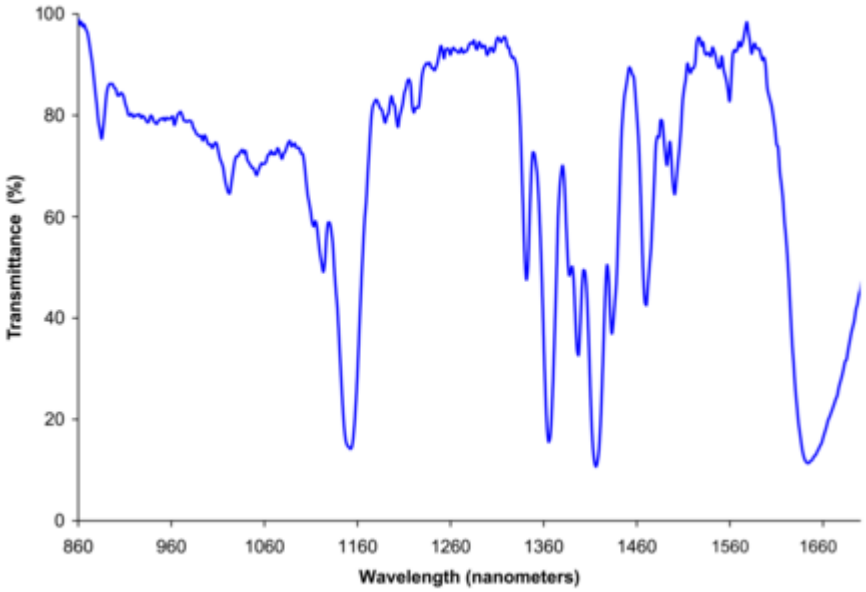
Why don't these molecules have a dipole moment?

_____

_____

_____

Generally stronger bonds absorb infrared of higher energy. These stronger bonds will absorb at a higher **wavenumber** which is the reciprocal of **wavelength**. This means that shorter wavelength infrared (which has higher energy) has a larger wavenumber. **See Table 7.6 on p.90 of the textbook.**



To convert a wavelength in nanometers (nm) to a wavenumber with units of cm^{-1} you must change the units for wavelength to cm and then take the reciprocal of that number. **In Figure 7.25 of the text wavelengths measured in µm (10^{-6} m) are converted to wavenumber by dividing the number by 10^4 to convert them to cm (10^{-2} m) and then taking the reciprocal.**

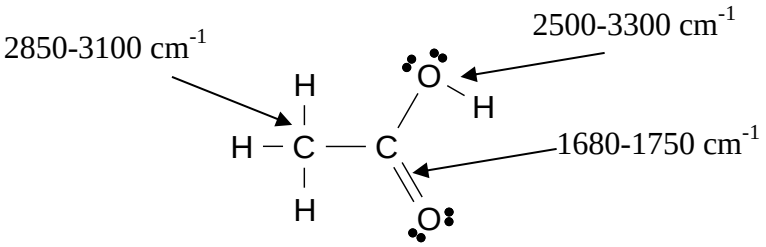
The sample cells in infrared spectroscopy must be made from salts such as NaCl and KBr because glass and plastic absorb infrared and interfere with the readings that would be taken

Table 7.8, p.93 – Characteristic Infrared Absorbance Bands

Bond	Location	Wavenumber (cm^{-1})

Note: smaller atoms in molecules require higher energy infrared light for absorption (see text p.90.)

Worked example 7.5 pp.93-94



Band A is O–H

Band B is C–H

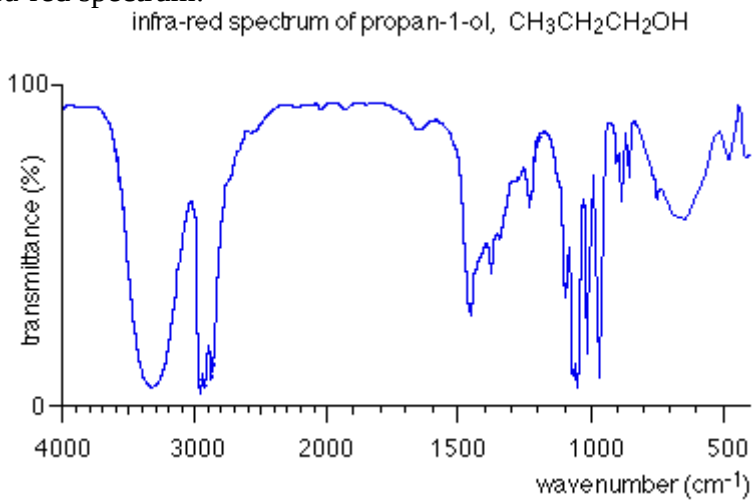
Band C is C=O

The Fingerprint Region of an Infra-red Spectrum

This page explains what the fingerprint region of an infra-red spectrum is, and how it can be used to identify an organic molecule.

What is the fingerprint region

This is a typical infra-red spectrum:



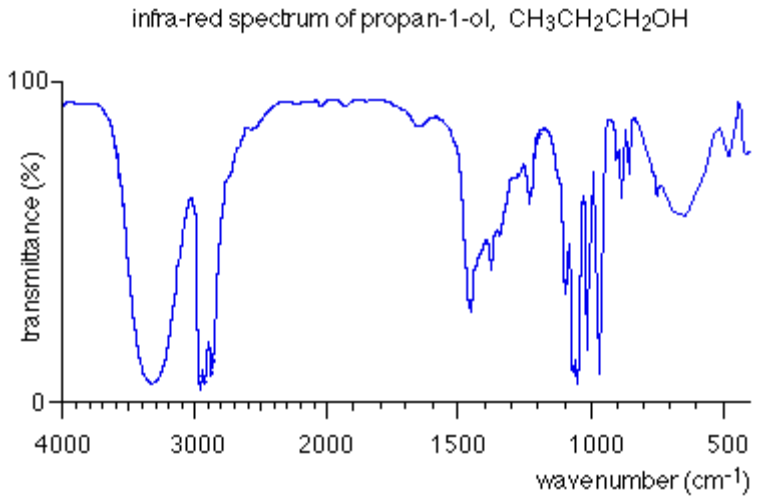
Each trough is caused because energy is being absorbed from that particular frequency of infra-red radiation to excite bonds in the molecule to a higher state of vibration - either stretching or bending. Some of the troughs are easily used to identify particular bonds in a molecule. For example, the big trough at the left-hand side of the spectrum is used to identify the presence of an oxygen-hydrogen bond in an -OH group.

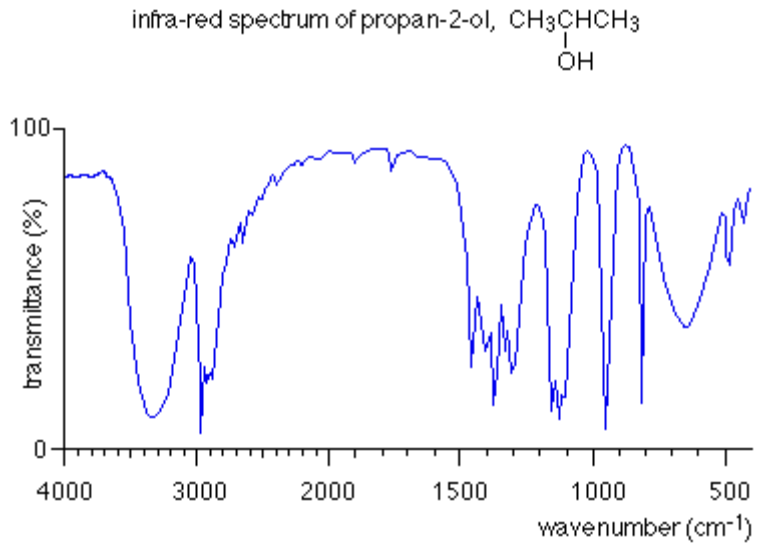
The region to the right-hand side of the diagram (from about 1500 to 500 cm^{-1}) usually contains a very complicated series of absorptions. These are mainly due to all manner of bending vibrations within the molecule. This is called the ***fingerprint region.***

It is much more difficult to pick out individual bonds in this region than it is in the "cleaner" region at higher wavenumbers. The importance of the fingerprint region is that each different compound produces a different pattern of troughs in this part of the spectrum.

Using the fingerprint region

Compare the infra-red spectra of propan-1-ol and propan-2-ol. Both compounds contain exactly the same bonds. Both compounds have very similar troughs in the area around 3000 cm^{-1} - but compare them in the fingerprint region between 1500 and 500 cm^{-1}.





The pattern in the fingerprint region is completely different and could therefore be used to identify the compound.

So . . . to positively identify an unknown compound, use its infra-red spectrum to identify what sort of compound it is by looking for specific bond absorptions. That might tell you, for example, that you had an alcohol because it contained an -OH group.

You would then compare the fingerprint region of its infra-red spectrum with known spectra measured under exactly the same conditions to find out which alcohol (or whatever) you had.

35 Exercise

Analysis of organic compounds by IR spectroscopy—data analysis

Purpose

Determine the identity of two colourless organic liquids from their IR spectrum.

Procedure

The labels have come off two bottles of colourless organic liquids. The labels read 'propanone' and 'propan-2-ol'. Propanone (acetone) is a commonly used solvent. It is a member of the ketone homologous series that contain a C=O functional group. Propan-2-ol is a member of the alkanol (alcohol) homologous series and contains the OH functional group. The structure of these two compounds is given in Figure 35.1.

Figure 35.1 Structure of **(a)** propan-2-ol and **(b)** propanone (acetone)

IR spectra of the two liquids will be used to assign each its correct label. Organic compounds will readily absorb infrared light. The wavelength of the light absorbed depends on the functional groups in the molecules. A number of functional groups such as the OH group and the C=O group give well-defined peaks at known wavelengths.

1 Calibrate the IR spectrometer first by running the spectrum of a pure polystyrene standard. A very sharp characteristic peak in the polystyrene is agreed by convention to fall at 1601 cm^{-1}.
2 Fill the liquid sample cell holder with 1–2 mL of the first liquid. IR light passes through the IR transparent window (e.g. KBr) and through the liquid into the detector. The spectra obtained are shown in Figure 35.2.

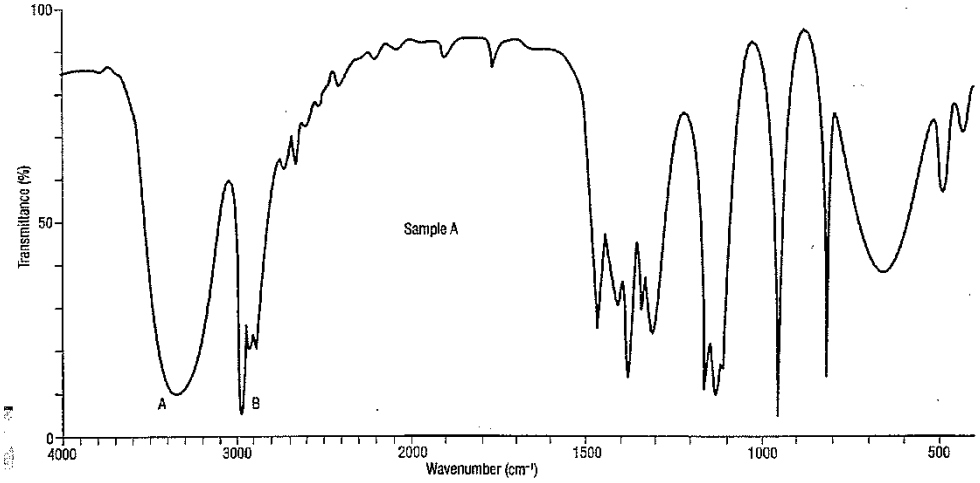


Figure 35.2 Spectra obtained from Sample A

3 Clean the cell thoroughly.
4 Analyse the second sample in the same way.

The spectra obtained are shown in Figure 35.3.

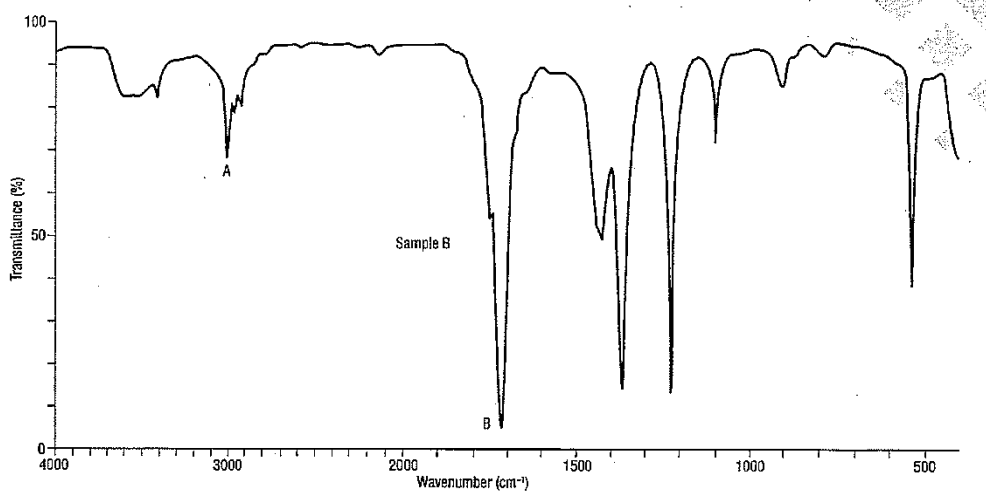


Figure 35.3 Spectra obtained from Sample B

The major peaks in the spectrum are identified by comparison with data tables. A simplified data table is given in Table 35.1.

Table 35.1 Major spectrum peaks

Wavenumber cm^{-1}	Phenomenon	Functional group
3600–3200	O–H stretch	Hydroxy
3000–2850	C–H stretch	Alkyl
1800–1680	C=O stretch	Carbonyl (aldehydes, ketones)
1670–1615	C=C stretch	Alkenes
1200–1070	C–O stretch	Ether

Table 35.2 Propanone

Group	Wavelength range cm^{-1}
C–H	3000–2850
C=O	

Table 35.3 Propan-2-ol

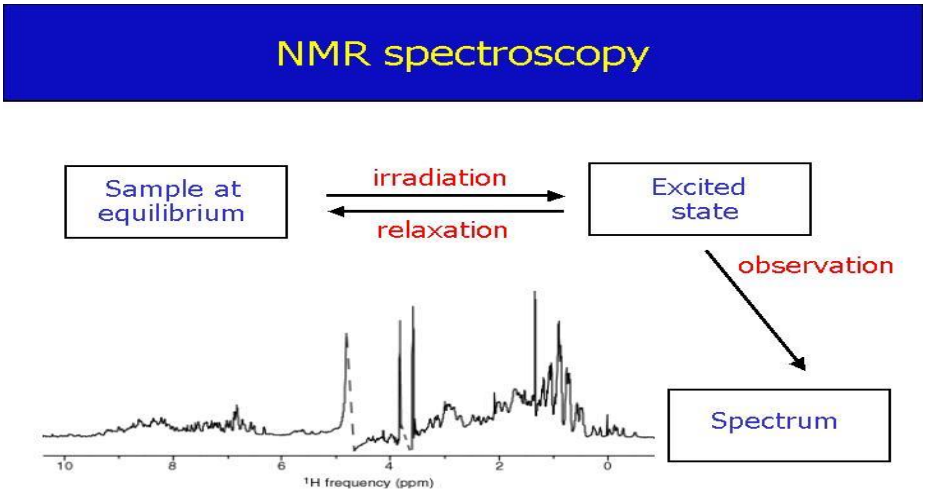
Group	Wavelength range cm^{-1}

Questions

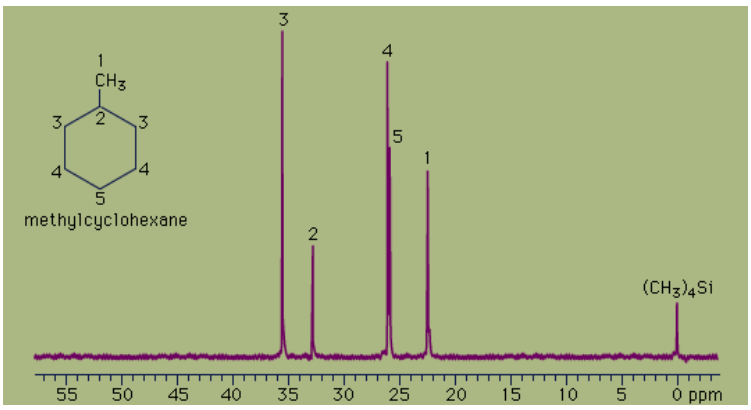
1 Look at the structure of the two compounds in Figure 35.1. Identify the main functional groups that you think would give rise to a peak in the infrared spectrum.
2 Complete Tables 35.2 and 35.3 for each compound. The first table has been partly completed for you.
3 Suggest possible identities to the peaks marked A and B on each spectrum by referring to Table 35.1.
4 Identify the compounds which gave Spectrum A and Spectrum B.

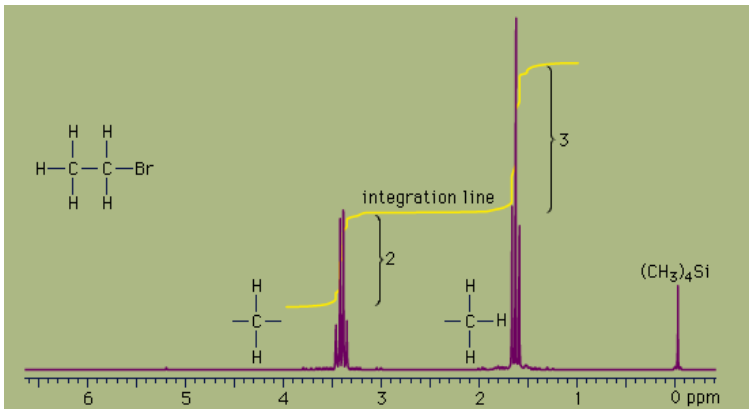
Nuclear Magnetic Resonance (NMR) – Text pp.97-101

NMR uses electromagnetic radiation from the radiowave section of the electromagnetic spectrum and external magnetic fields. Radiowaves are low energy and therefore do not affect electrons and chemical bonds. The radiowaves cause changes in the "spin" of nucleons (neutrons and protons) in an atom. Only atoms with odd numbers of nucleons produce nuclear "spins" that can be analysed with NMR. Commonly, ^{1}H and ^{13}C are analysed because these 2 elements are found in many organic (carbon based) compounds.**Nuclei with an overall spin behave like tiny magnets that can be analysed if they are exposed to an external magnetic field.**



When a strong external magnetic field is applied to a nucleus nucleons split into 2 different energy levels. The difference in these energy leveles corresponds to photons of energy from the radio region of the electromagnetic spectrum. Radiowaves can be absorbed by nuclei in these circumstances and can produce NMR spectra such as these:





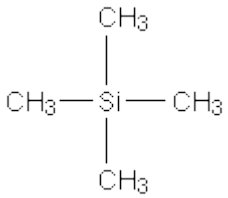
NMR Method

- The sample and solvent mixture are tube that spins to ensure that the contents are exposed to a uniform magnetic field.
- The tube is placed between the poles of a powerful magnet and a strong magnetic field is applied.
- The sample is then exposed to short, powerful bursts of radiowaves set at specific wavelengths.
- The wavelength of the radiowaves is usually kept constant and the sample is exposed to a range of applied magnetic field strengths.
- At specific magnetic field strengths, 1H and 13C nuclei in particular environments, absorb the applied radiowaves and move to higher energy levels. This is called **resonance**.
- The absorption is detected and plotted on a graph that compares the magnetic field strength causing resonance to the intensity of the absorption signal.

The need for a standard for comparison - TMS

Before we can explain what the horizontal scale means, we need to explain the fact that it has a zero point - at the right-hand end of the scale. The zero is where you would find a peak due to the carbon-13 (when conducting ^{13}C NMR analysis) and hydrogen-1 (when conducting ^{1}H NMR analysis) atoms in ***tetramethylsilane*** - usually called ***TMS.*** Everything else is compared with this.

Tetramethylsilane is chemically inert
and therefore will not react with

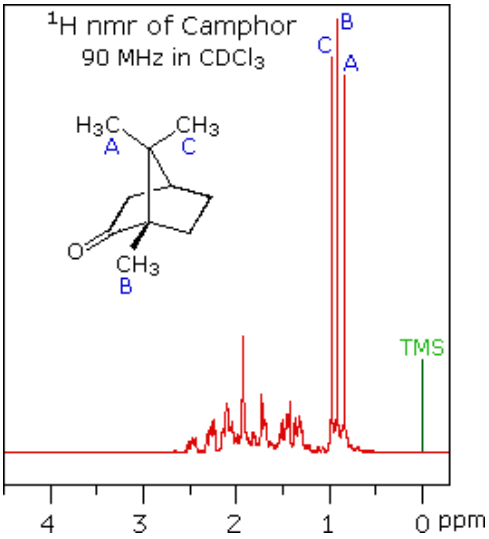


You will find that some NMR spectra show the peak due to TMS (at zero), and others leave it out. Essentially, if you have to analyse a spectrum which has a peak at zero, you can ignore it because that's the TMS peak.

TMS is chosen as the standard for several reasons. The most important are:

- It has 4 carbon atoms, and 12 hydrogen atoms, all of which are in exactly the same environment. They are joined to exactly the same things in exactly the same way. That produces a single peak, but it's also a strong peak (because there are lots of carbon and hydrogen atoms all doing the same thing).
- The electrons in the C-Si bonds are closer to the carbons in this compound than in almost any other one. That means that these carbon nuclei are the most shielded from the external magnetic field, and so you would have to increase the magnetic field by the greatest amount to bring the carbons back into resonance.

  The net effect of this is that TMS produces a peak on the spectrum at the extreme right-hand side. Almost everything else produces peaks to the left of it.



The chemical shift

The horizontal scale is shown as δ(ppm). δ is called the ***chemical shift*** and is measured in ***parts per million*** - ppm. A peak at a chemical shift of, say, 60 means that the carbon atoms which caused that peak need a magnetic field ***60 millionths less*** than the field needed by TMS to produce resonance. A peak at a chemical shift of 60 is said to be ***downfield*** of TMS. The further to the left a peak is, the more downfield it is.

Solvent
The solvent is chosen as a chemical that will not produce a signal on the NMR spectrum. **Refer to p.99 and record some examples of suitable solvents and explain why they are suitable.**

_____

_____

_____

_____

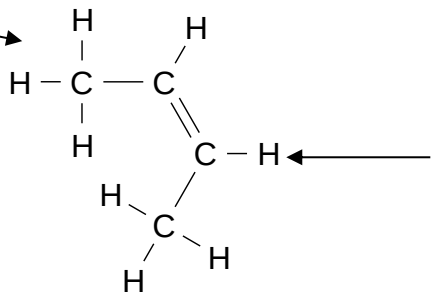
Nuclear shielding
The most important aspect of the NMR frequency used for applications of NMR is the 'shielding' effect of the surrounding electrons. In general, this electronic shielding reduces the magnetic field *at the nucleus* (which is what determines the NMR frequency). As a result the energy gap is reduced, and the frequency required to achieve resonance is also reduced. This shift of the NMR frequency due to the chemical environment is called the chemical shift, and it explains why NMR is a direct probe of chemical structure.

Basically, shielding electrons will block some of the external magnetic field which means the the strength of this magnetic field needs to be increased to get the nuclei "resonating" (magnetically shifting). In polar bonds electrons can be drawn away from ^{13}C and ^{1}H nuclei which will decrease shielding. Multiple peaks appear on an NMR spectrum when many different magnetic field strengths are required to produce resonance.

Proton NMR peak splitting
Fig 7.6 on p.101 – NMR peaks can be split by neighbouring atoms. In proton NMR this peak splitting is caused by neighbouring protons. The "n + 1" rule applies to determine the number of splits that will occur to a peak where "n" equals the number of protons bonded to neighbouring atoms.

Two different "proton environments" exist in 2-butene. A proton NMR spectrum will therefore have 2 peaks. With higher sensitivity these peaks split due to the numbers of neighbouring protons.

The CH_3 peak will split into 2 peaks as CH_3 is bonded to CH (n + 1 = 2).



The CH peak will split into 4 peaks as CH is bonded to CH_3 (n + 1 = 4).

Note: protons (H) in equivalent environments do not cause splitting of their own peak ie. the 2 CH protons do not cause splitting in their own peak even though they are

Relative Peak Area
This equals the number of protons in that environment:

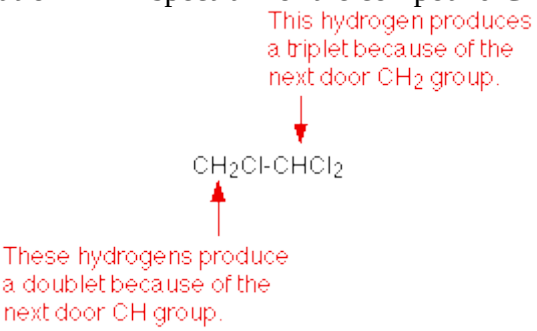
CH_3 has a relative peak area of 3
CH_2 has a relative peak area of 2
CH has a relative peak area of 1

Note: the H in OH does not split the peaks of adjacent H atoms, nor is its own peak split – p.100 of text.

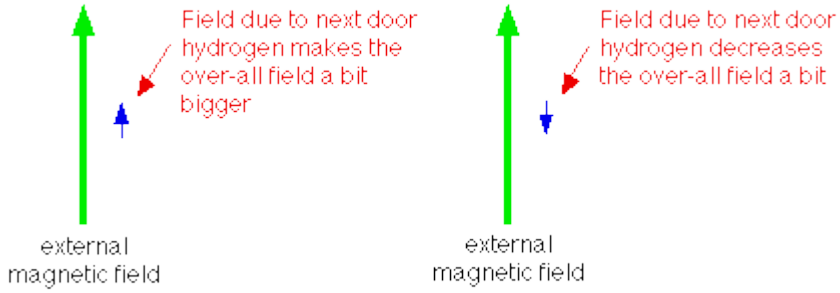
Spin-spin coupling

The origin of a doublet

Consider what the high resolution NMR spectrum of the compound $CH_2Cl\text{-}CHCl_2$ would look like.



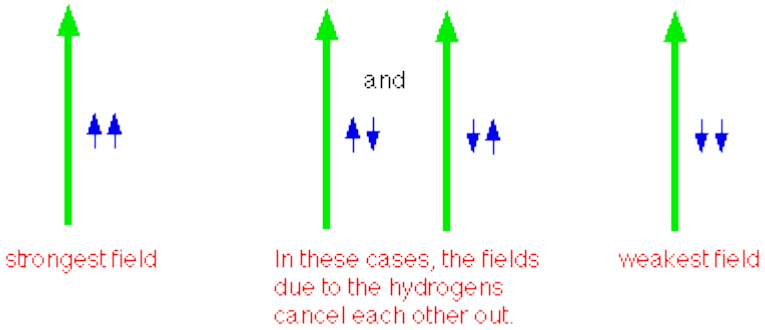
Focus on the CH_2 group. Why is that a doublet? Remember that the peaks in an NMR spectrum are in different places because the hydrogens are experiencing different magnetic fields due to their different environments. Two peaks close together must mean that those particular hydrogens are experiencing two slightly different magnetic fields. Those two slightly different fields are caused by the hydrogen in the CH group next door. The hydrogen next door has a small magnetic field of its own, which could be aligned with the external magnetic field or opposed to it. Depending on which way around it is aligned, it will either strengthen or weaken the field felt by the CH_2 hydrogens.



There is an equal chance of either of these arrangements happening and so there will be two peaks due to the CH_2 hydrogens, close together and with equal areas under them (because of the 50/50 chance of either arrangement).

The origin of a triplet

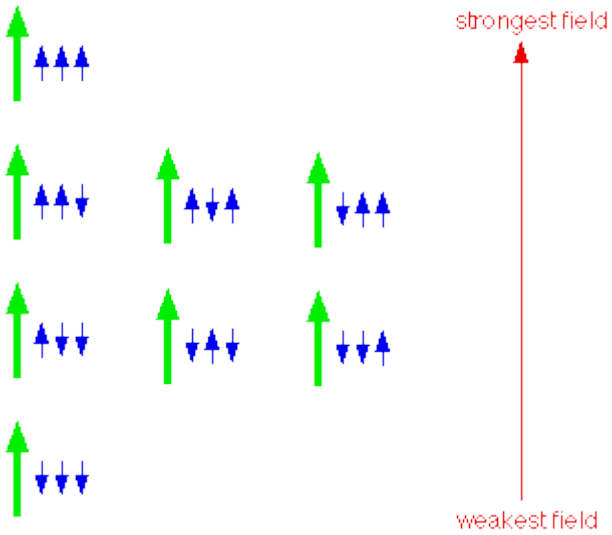
Now focus on the CH group in the compound $CH_2Cl\text{-}CHCl_2$. Why is that a triplet? It must be a triplet because that hydrogen is experiencing any one of three slightly different magnetic fields. Think about the magnetic alignments of the hydrogens on the next door CH_2 group. These are the various possibilities:



The two arrangements in the centre of the diagram produce the same field (exactly the same as the external field). So . . . there are three possible magnetic fields that the CH hydrogen could feel, and so there are three peaks close together - a triplet. The areas under the peaks are in the ratio of 1:2:1 because that represents the chances of these various magnetic fields occurring.

The origin of a quartet

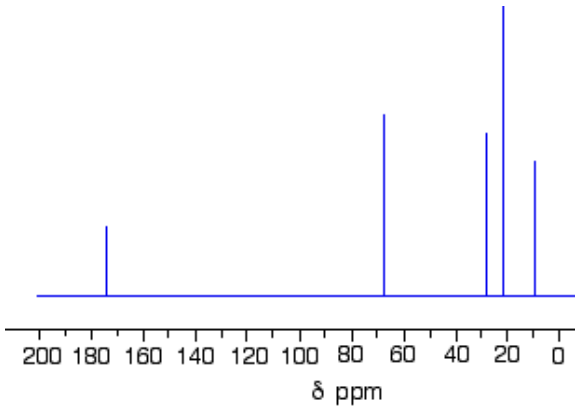
If you apply the same sort of argument to hydrogens next door to a CH_3 group, you will find that they could be experiencing any one of four different magnetic fields depending on the alignment of the CH_3 hydrogens.



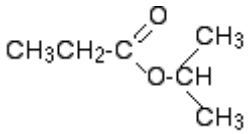
All the arrangements in the second line produce the same field. All the alignments in the third line also produce the same field, but this time a bit smaller. There are four different possible fields, with the chances of them arising in the ratio 1:3:3:1. So a CH_3 group produces a quartet in the spectrum of the hydrogens of the next door group, with the peak sizes in the ratio 1:3:3:1.

The C-13 NMR spectrum for a more complicated compound

This is the C-13 NMR spectrum for 1-methylethyl propanoate (also known as isopropyl propanoate or isopropyl propionate).



This time there are 5 lines in the spectrum. That means that there must be 5 different environments for the carbon atoms in the compound. Is that reasonable from the structure?



Well - if you count the carbon atoms, there are 6 of them. So why only 5 lines? In this case, two of the carbons are in exactly the same environment. They are attached to *exactly* the same things. Look at the two CH_3 groups on the right-hand side of the molecule.

You might reasonably ask why the carbon in the CH_3 on the left isn't also in the same environment. Just like the ones on the right, the carbon is attached to 3 hydrogens and another carbon. But the similarity isn't *exact* - you have to chase the similarity along the rest of the molecule as well to be sure.

The carbon in the left-hand CH_3 group is attached to a carbon atom which in turn is attached to a carbon with two oxygens on it - and so on down the molecule.

That's not *exactly* the same environment as the carbons in the right-hand CH_3 groups. They are attached to a carbon which is attached to a single oxygen - and so on down the molecule.

All you need to realise is that each line in a C-13 NMR spectrum recognises a carbon atom in one particular environment in the compound. If two (or more) carbon atoms in a compound have *exactly* the same environment, they will be represented by a single line.

Internet Data Base of NMR Spectra (Google search sdbs)

The following internet site: http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng lists spectra for a large number of compounds.You can search for the spectra of compounds using their names, molecular formulas and molecular weight (by name is the easiest).

36 Exercise

Interpretation of the nuclear magnetic resonance (NMR) spectra of a number of organic compounds—data analysis

Purpose

To match key features of the NMR spectrum to the structural features of some simple organic compounds.

Theory

Protons in the samples analysed by H (proton) nuclear magnetic resonance spectrometry release energy when they move from a high to low 'spin' state. The energy released is shown as a peak on the spectrum. The same principle applies to ^{13}C NMR. The following information can be gleaned from these peaks in a proton NMR spectrum:

- chemical shift—the energy of the peak compared to a standard is called the chemical shift and gives information about the functional group the H is attached to. A table of chemical shifts is provided in *Heinemann Chemistry 2*, Table 7.9.
- peak splitting—the number of fine peaks each major peak is split into gives information about the neighbouring protons.
- peak areas—the total area of each major peak of peak cluster gives information about number of equivalent hydrogens in the molecule.
- the number of peak sets—hence the number of different environments of H's. Refer to Table 36.1

Often a number of spectroscopic techniques are used to determine the identity of a sample. The sample used to obtain the results in Figure 36.1 has been analysed by mass spectrometry and infrared spectroscopy giving information about the mass of the molecules as well as functional groups present (^1H proton). Nuclear magnetic resonance spectra have been given to distinguish between alternative structures for the sample.

Table 36.1 Relationship between shape of peak and number of H atoms

Number of H atoms on adjacent C atoms	Shape of peak
0	Single peak
1	Double peak
2	Triple peak
3	Quadruple peak

Table 36.2 Butan-2-one

Group (with same H environment)	Relative abundance	Splitting

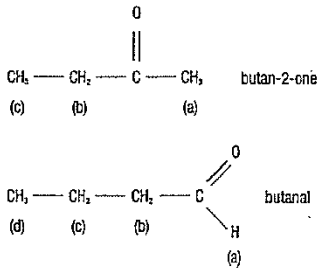


Figure 36.1 Butan-2-one and butanal

Table 36.3 Butanal

Group (with same H environment)	Relative abundance	Splitting

Data

The sample has been analysed by mass spectrometry and found to have a relative molecular mass of 72. IR spectroscopy shows a strong absorption band at 1718 cm^{-1}, which is likely to be due to C=O stretching in a ketone or an aldehyde. There are two compounds, butan-2-one and butanal, that match this data. The identity of the compound can be determined by analysis of the proton NMR spectrum.

Questions

1 Look at the structure of butan-2-one and identify:
   a the number of different H environments
   b number of H's in each environment
   c the number of fine peaks each would be split into (complete Table 36.2):
2 Look at the structure of butanal and identify:
   a the number of different H environments
   b the number of H's in each environment
   c the number of fine peaks each would be split into (complete Table 36.3):

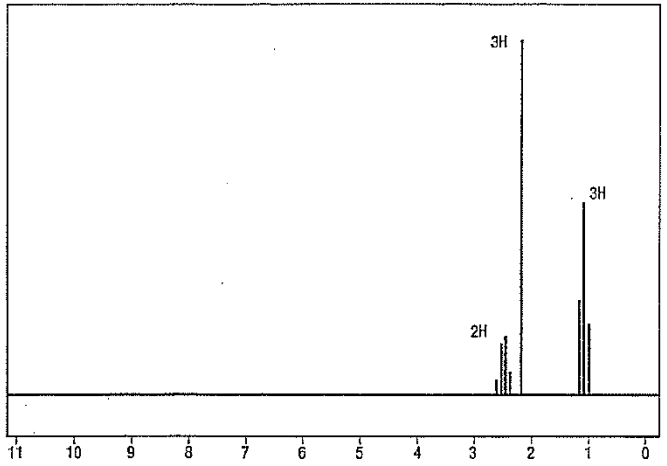


Figure 36.2 ^1H NMR spectrum of unknown compound

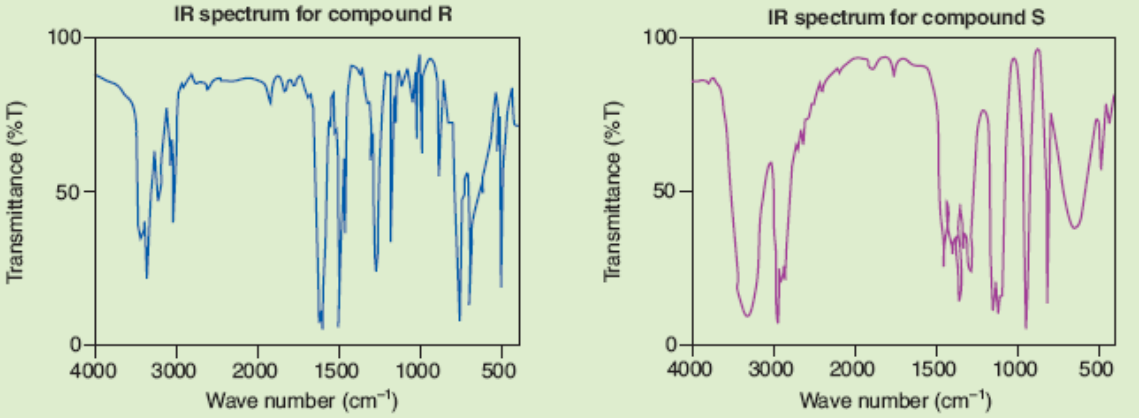
3 Complete Table 36.4 for the ^1H NMR spectrum. The relative number of H's is indicated on the spectrum.

Table 36.4 ^1H NMR spectrum

Chemical shift	Relative abundance	Splitting	Group

4 Identify the unknown compound.
   ^{13}C NMR spectroscopy is also used to identify organic compounds.
5 How many peaks would you expect in ^{13}C NMR of:
   a butan-2-one?
   b butanal?
6 How can ^{13}C NMR spectroscopy be used in distinguishing between butan-2-one and butanal?
7 How do the proton and ^{13}C NMR spectra of butan-2-one differ?

17. Forensic chemists often use infra-red spectra to identify organic bases such as amines, which have an —NH_2 group. The —N—H functional group produces peaks at 3200–3500 cm^{-1} and at 1560–1650 cm^{-1}. Which of the following spectra, R or S, is the amine?



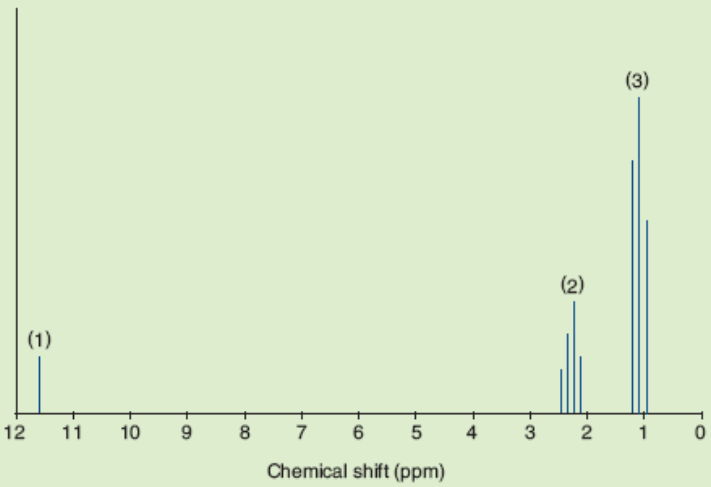
Answer:

21. Shown at right is an NMR spectrum of a molecule with the molecular formula $C_3H_6O_2$.

(a) Identify the peaks using the table of chemical shifts (table 5.6).

(b) How many peaks would you most likely find in the set of peaks for the CH_2 group?

(c) Sketch the structure of the molecule.



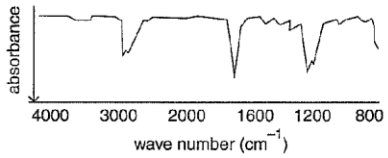
(a)

(b)

(c)

Question 1.3.13

Infrared spectroscopy may be used to determine the functional groups present in an organic compound. A simplified infrared spectrum of one compound is shown below.



a. Why is water an unsuitable solvent for infrared spectroscopy?

1 mark

b. What wave number (in cm^{-1}) would a wavelength of 10 μm correspond to?

1 mark

c. Based on the infrared spectrum shown above,

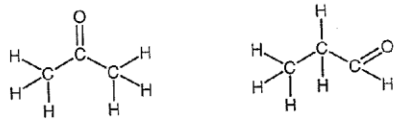
i. suggest two bonds that are likely to be present in the compound.

ii. suggest two bonds that are unlikely to be present in the compound.

2 + 2 = 4 marks

Question 1.3.14

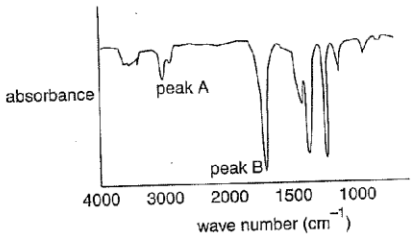
Compounds with the molecular formula C_3H_6O were investigated using infrared and ^1H nuclear magnetic resonance spectroscopy. Two possible structures for the compounds are shown below.



propanone

propanal

a. The infrared spectrum of propanone is shown below.



Identify the bond type responsible for

i. peak A.

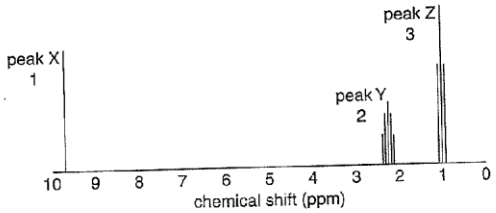
ii. peak B.

1 + 1 = 2 marks

b. Explain why a sample cell used in infrared spectroscopy cannot be made from glass or plastic.

1 mark

c. The ^1H NMR spectrum of propanal is shown below. The numbers beside the peaks show the relative peak areas.



i. Identify the type of ^1H nucleus (CHO, CH_2 or CH_3) responsible for peak X.

ii. Explain why peak Z is split into a triplet.

1 + 2 = 3 marks

d. How many peaks would be expected on the

i. ^1H NMR spectrum of propanone.

ii. ^{13}C NMR spectrum of propanone.

iii. ^{13}C NMR spectrum of propanal.

1 + 1 + 1 = 3 marks

e. To standardise measurements made on different instruments and under different conditions in ^1H NMR spectroscopy, a reference compound is used. TMS (tetramethylsilane) is often chosen.

State one reason why TMS is a suitable reference compound for ^1H NMR spectroscopy.

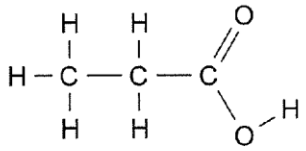
1 mark

Answers

Q.17 R is the amine as it shows an obvious absorbance peak at 1560-1650 cm-1. This peak is not evident on the spectrum for compound S.

Q.21 (a) R–CH3 (0.9 ppm), R_2–CH_2 (1.3 ppm: note this peak has moved up the scale on this particular spectrum), R–COOH (11.5 ppm).
(b) since there is a CH_3 group next to the CH_2 group 4 peaks can be expected
ie. n + 1 = 3 + 1 = 4

(c)



Question 1.3.13

a. Water itself is a strong infrared absorber.

b. $10\ \mu m = 10 \times 10^{-6}\ m = 10^{-5}\ m$

$$\text{wave number} = \frac{1}{\text{wavelength}} = \frac{1}{10^{-5}} = 10^5\ m^{-1}$$

$$= 1000\ cm^{-1}$$

c. **i.** The peak at approximately 1700 could be a C=O bond. The peak at 1200 could be a C–O bond. Most organic compounds would be expected to have C–H bonds. The peak at 2800 could be an O–H (acid) bond.

ii. The absence of a peak in the 3000–3500 range suggests that no O–H (alcohol) or N–H (amine) bonds are present.

Question 1.3.14

a. **i.** C–H

ii. C=O

b. Glass and plastic both absorb infrared radiation.

c. **i.** CHO

ii. Peak Z, with a relative peak area of 3, is due to the CH_3 nuclei. This peak is therefore split into three peaks (2 + 1) due to the two neighbouring CH_2 nuclei.

d. **i.** 1
(the six CH_3 protons are equivalent)

ii. 2
(the two CH_3 carbons are equivalent)

iii. 3

e. For example:
TMS is chemically inert and so will not react with the sample.
TMS produces a single peak well away from most of the peaks of interest to organic chemists.

Nuclear Magnetic Resonance Spectroscopy Worksheet

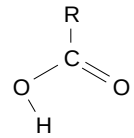
Nine compounds are drawn on the following page. The NMR spectrum for each is among the nine spectra on the next 3 pages.

1) Match each compound with its NMR.

2) Draw the structure above the corresponding spectrum and show clearly which NMR peak corresponds to which proton(s) in the molecule.

Steps in analyzing an NMR spectrum.

1. Look for any proton environment/s that will give an obvious peak eg: the carboxyl proton at 11.5 ppm.



$CH_3CH_2CO_2H$

propanoic acid

Will have a distinctive peak at 11.5 ppm.

2. Determine the number of H environments and hence the number of peaks that will appear on the readout.

3 proton environments

$CH_3CH_2CO_2H$

propanoic acid

3. Determine the number of peak splits that each H environment will have using the n+1 rule.

n + 1 = 3 n + 1 = 4 n + 1 = 1

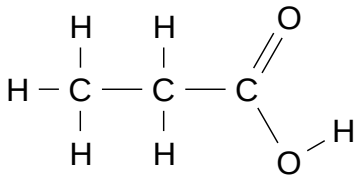
$CH_3CH_2CO_2H$

propanoic acid

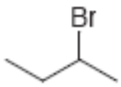
A relative peak size of 3 indicates 3 H in this environment. 3 peak splits indicates 2 neighbouring protons (CH_2). Peak shift of 0.9 ppm indicates a RCH_3 proton

A relative peak size of 2 indicates 2 H in this environment. 4 peak splits indicates 3 neighbouring protons (CH_3). Peak shift of 2.4 ppm indicates a CH_2 proton

Peak shift of 11.5 ppm indicates a COOH proton environment. A relative peak size of 1 indicates a single H in this environment. A single peak indicates no neighbouring protons.



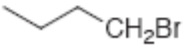
The NMR spectrum for propanoic acid has 3 major peaks due to 3 different proton (H) environments.



2-bromobutane

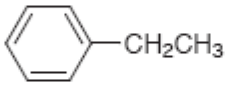
CH_3CH_2OH

ethanol

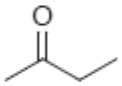


1-bromobutane

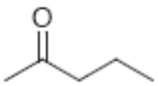
1-pentene



ethylbenzene



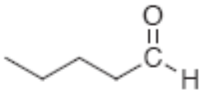
2-butanone



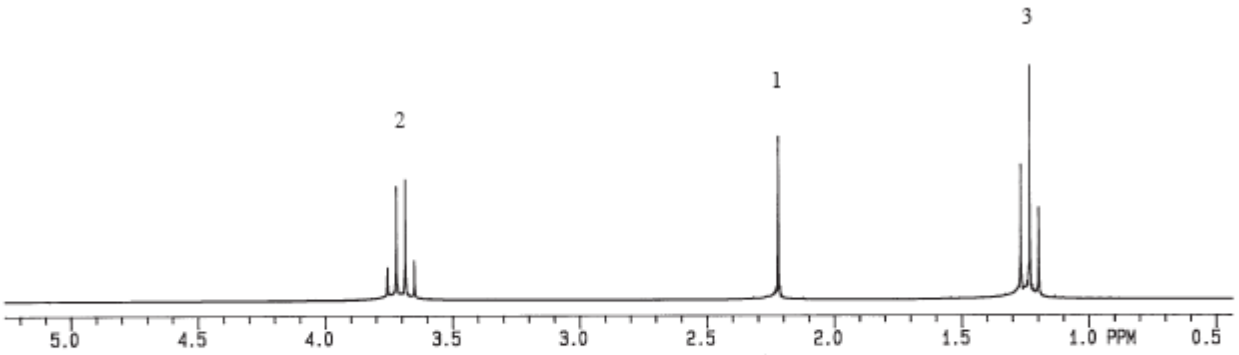
2-pentanone

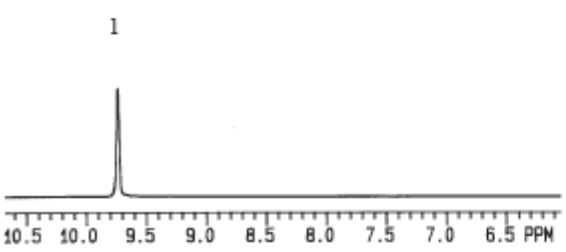
$CH_3CH_2CO_2H$

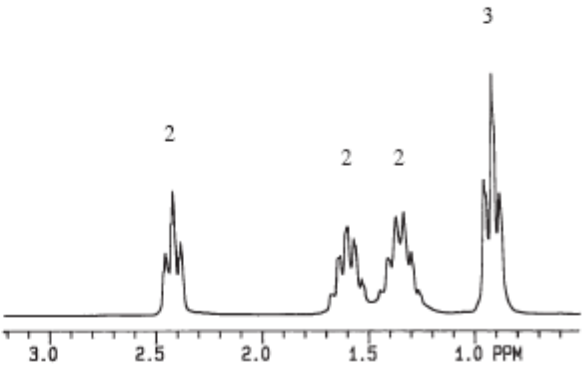
propanoic acid

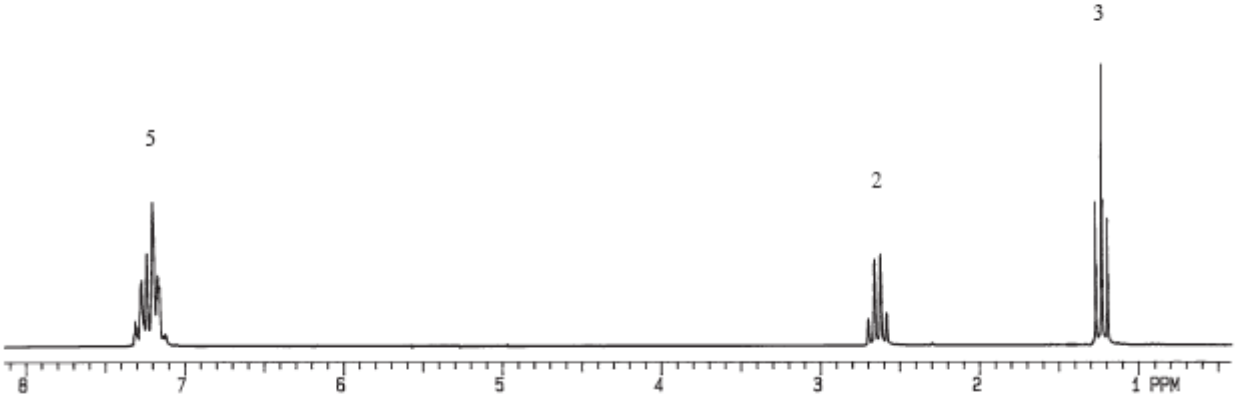


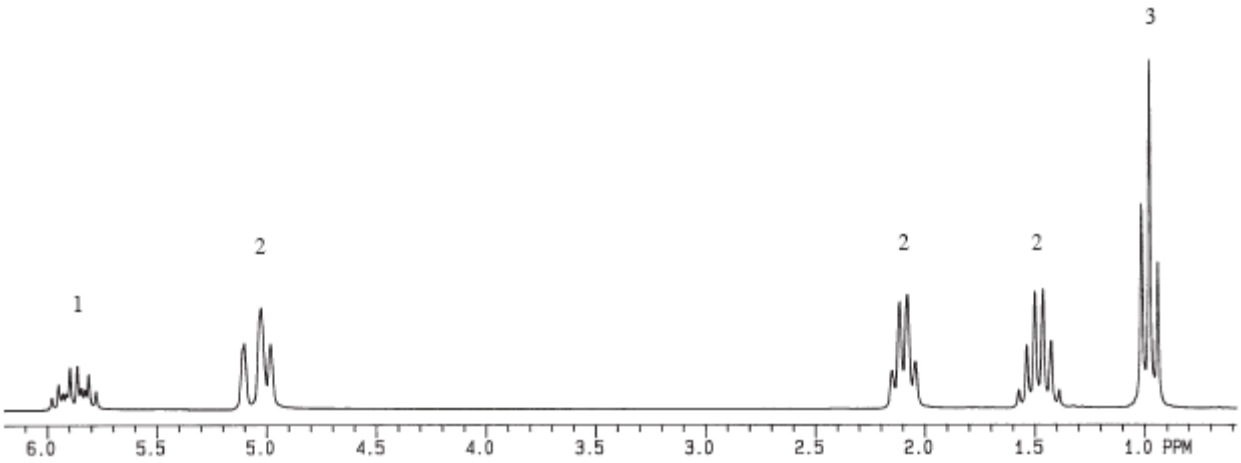
pentanal

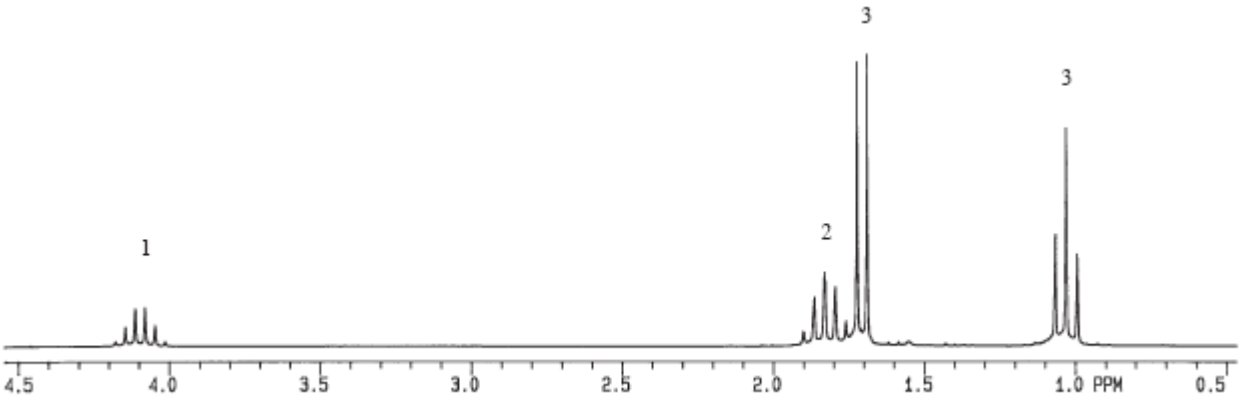


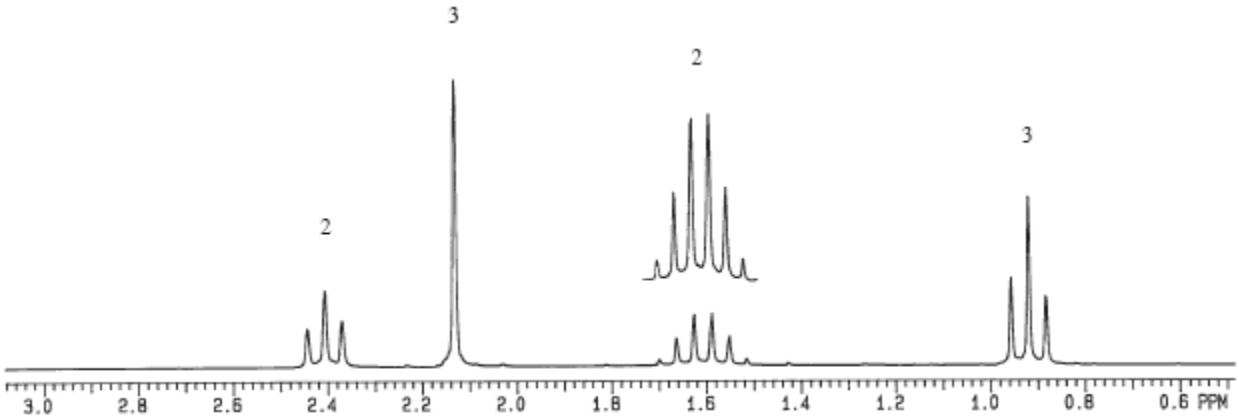


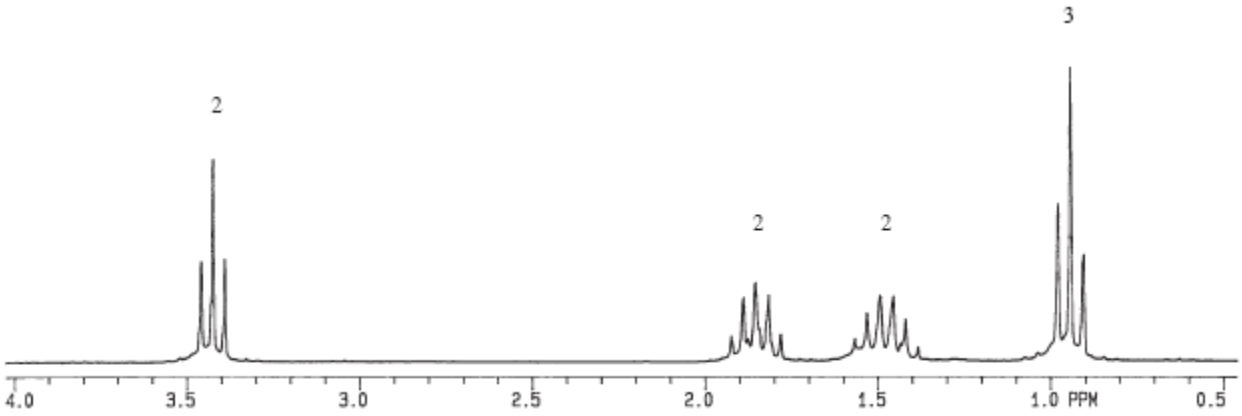


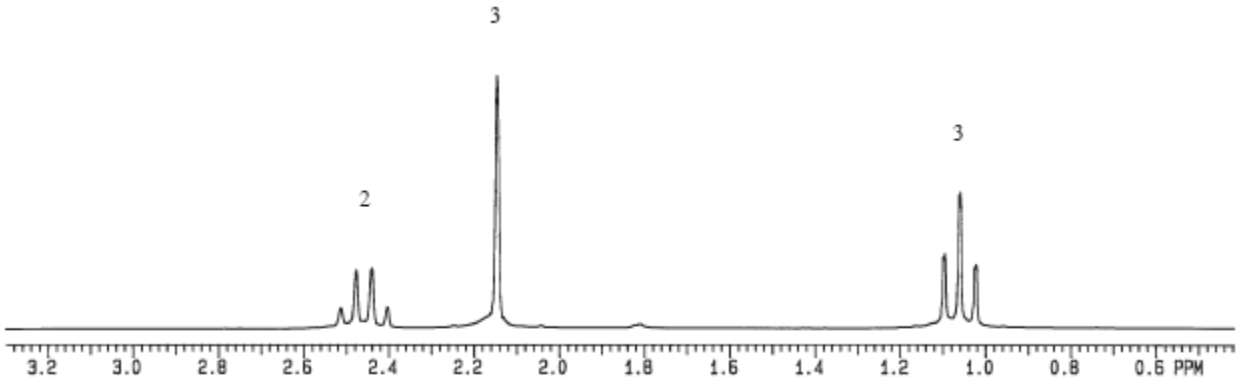

5
2
3
8
7
6
5
4
3
2
1 PPM


1
2
2
2
3
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0 PPM


1
2
3
3
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0 PPM
0.5


2
3
2
3
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6 PPM


3
2
2
2
4.0
3.5
3.0
2.5
2.0
1.5
1.0 PPM
0.5


3
3
2
3.2
3.0
2.8
2.6
2.4
2.2
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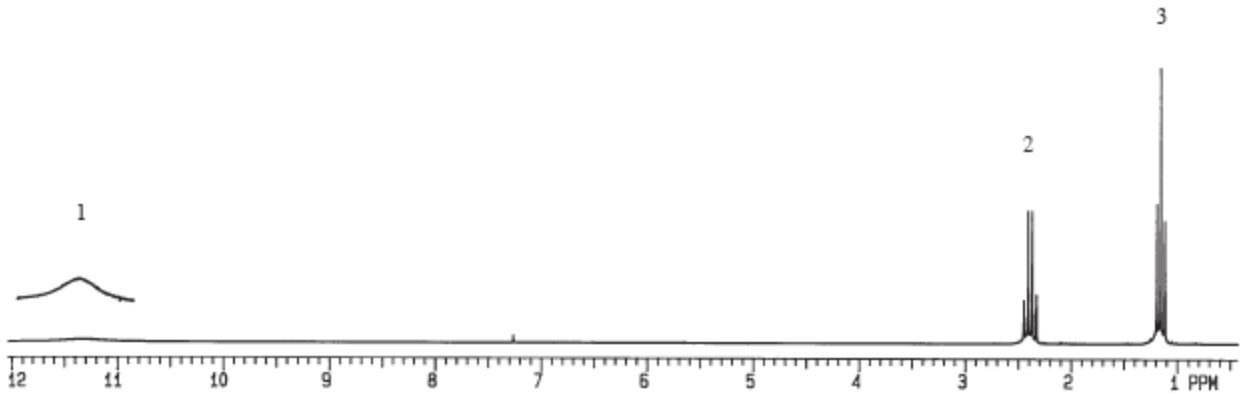
1.8
1.6
1.4
1.2
1.0
0.8
0.6 PPM


3
2
1
12
11
10
9
8
7
6
5
4
3
2
1 PPM

Mass Spectrometry

Key Concepts

- The sample, as a gas, enters the evacuated tube.
- Positive ions are formed in the ionisation chamber when an electron beam dislodges electrons from the sample atoms or molecules.
- The positive ions are accelerated by an electric field.
- The ions enter a magnetic field perpendicular to their path. This causes the ions to move in a curved path with a radius that depends upon the mass to charge ratio (*m*/*e*) of the ions.
- Only ions moving in a curved path of a particular radius, corresponding to a fi xed *m*/*e* ratio, will reach the collector.
- Particles of different *m*/*e* ratio are able to reach the collector through adjustments to the accelerating voltage or the strength of the magnetic fi eld.
- The collector measures the current due to the ions reaching the detector and the data is recorded as a mass spectrum.

Mass spectrometry (MS) is an analytical technique that measures the **mass-to-charge ratio** of charged particles. It is used for determining masses of particles, for determining the elemental composition of a sample or molecule, and for elucidating the chemical structures of molecules, such as peptides and other chemical compounds. MS works by ionizing chemical compounds to generate charged molecules or molecule fragments and measuring their **mass-to-charge ratios**. In a typical MS procedure:

1. A sample is loaded onto the MS instrument and undergoes **vaporization**
2. The components of the sample are ionized by one of a variety of methods (e.g., by impacting them with an **electron beam**), which results in the formation of charged particles (ions)
3. The ions are separated according to their **mass-to-charge ratio** in an analyzer by electromagnetic fields
4. The ions are detected, usually by a quantitative method
5. The ion signal is processed into mass spectra

The technique has both qualitative and quantitative uses. These include identifying unknown compounds, determining the isotopic composition of elements in a molecule, and determining the structure of a compound by observing its fragmentation.

Parent Peak: the peak from the ion formed when a molecule loses a single electron – this identifies the molecule's molar mass.

Base Peak: the highest peak (most intense peak) it identifies the most common fragment produced during mass spectrometer analysis.

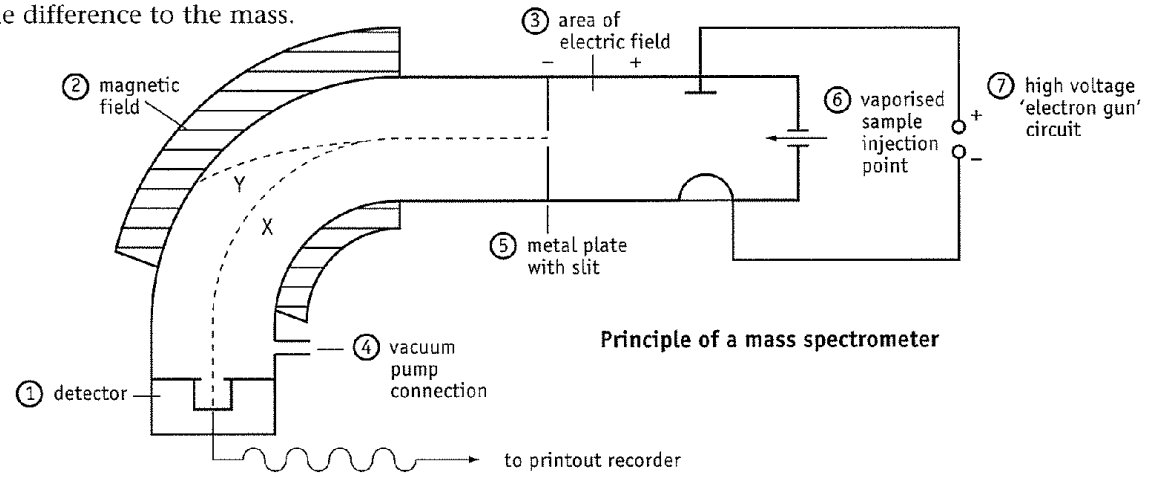
Heavy Isotopes: H_2O has a molar mass of 18 $gmol^{-1}$. It would be expected that the parent peak on a mass spectrum would appear at an *m/e* ratio of 18. Some questions will include odd peaks such as an *m/e* of 20. **See Q.5 on p.114 – The peaks at *m/e* 19 & 20 in this question are attributed to H_2O containing the heavy oxygen isotope with a RAM of 18.**

2 Atomic structure

Isotopes and relative atomic mass (cont.)

Measuring relative atomic mass

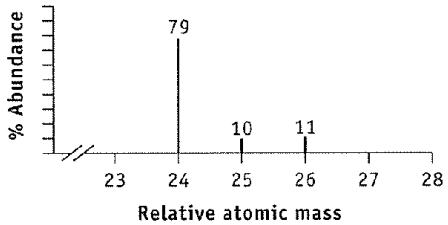
- The *mass spectrometer* is the instrument used to separate different atoms and measure their relative atomic masses. The instrument actually compares the masses of ions which have one positive charge, e.g. Ne^+. This is effectively the same as comparing atomic masses because losing an electron makes very little difference to the mass.



Principle of a mass spectrometer

- The magnetic field deflects ions in the beam into a detector at the end of the tube. Lighter ions are deflected more easily than heavier ions.
- The strength of the magnetic field is gradually increased so that ions of increasing mass enter the detector.
- The mass of an ion is indicated by the strength of the magnetic field needed to deflect it into the detector.
- The greater the number of ions hitting the detector at any time, the greater the output signal from the detector.
- A mass spectrometer printout shows: 1. the relative atomic mass of each type of atom;
  2. the percentage number of each type of atom.
- The average mass of isotopes of an element can be calculated from mass spectrometer readings.

Example: Mass spectrometer printout for magnesium



Calculation of average A_r of magnesium isotopes:

$$\text{Average} = \frac{79}{100} \times 24 + \frac{10}{100} \times 25 + \frac{11}{100} \times 26$$

$$= 18.96 + 2.5 + 2.86$$

$$= 24.32$$

4 Refer to the mass spectrometer diagram above.

(a) Identify by number the part of the mass spectrometer which:

(i) forms positive ions by bombarding the sample with high speed electrons _____

(ii) accelerates the positive ions _____

(iii) narrows positive ions into a beam _____

(iv) deflects positive ions _____

(b) Why must the tube be evacuated before the sample is introduced?

_____

(c) Which beam contains heavier particles, X or Y? _____

5 The three naturally occurring isotopes of neon have relative atomic masses of 22, 21 and 20. The percentage of these isotopes is 9.2%, 0.3% and 90.5%, respectively.

(a) Write symbols for each of these neon isotopes.

(b) Calculate the average relative atomic mass of neon.

6 Copper has two naturally occurring isotopes with relative atomic masses of 63 and 65. The average relative atomic mass for copper is 63.5. Write the symbol for the more abundant copper isotope. _____

The Mass Spectrometer

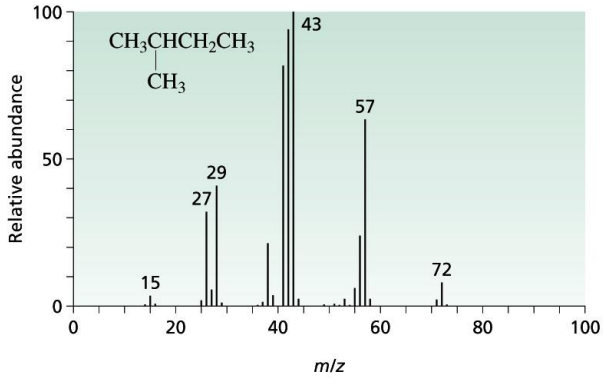
Introductory information

- The Mass Spectrometer separates atoms and molecules on the basis that they have different masses.
- It does this by turning atoms and molecules into positive ions ie. knocking an electron off the atom.
- These ions are sped up by negatively charged plates (the negative charge attracts the positive ions).
- These ions are passed through a magnetic field and they are deflected because moving electrically charged particles produce their own magnetic field.

Determining an unknown RAM

Basically, the amount that a particle is deflected by the Mass Spectrometer is used to determine its mass with reference to another particle with known mass eg. carbon-12, and the amount that carbon-12 is deflected.

Determining Masses of Particles



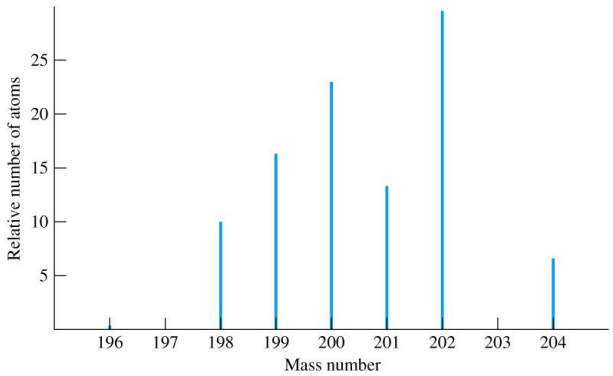
A compound such as 2-methylbutane can be analysed in a Mass Spectrometer. As it is ionised by a high voltage electron stream it can be broken up into smaller fractions eg. the peak height at m/z 15 is CH_3, m/z 72 is the whole compound, and m/z 29 would be a CH_3CH_2 fragment.

m/z 27 is

m/z 43 is

m/z 57 is

Calculating the RAM of Mercury (Hg)



This is a mass spectrum of mercury (Hg).

How many isotopes appear on the mass spectrum?

The relative abundance (% abundance) for each isotope can be calculated by comparing the peak heights of each isotope against the total of all the peak heights added together. The peak heights are measured by a detector which records the number of ions hitting it, and hence the electrical current that these ions produce.

Total Peak Height = 100

Mass Number	Peak Height	% abundance (% of total peak height)
198		
199		
200		
201		
202		
204		

RAM(Hg) = _____ = a.m.u

100

37 Exercise

Interpretation of the mass spectra of a number of organic compounds—data analysis

Purpose

In this exercise you will match the key features of the mass spectrum to the structural features of some simple organic compounds.

Theory

Mass spectrometry is used for the qualitative analysis of a number of simple organic compounds. The identity of the compounds can be determined from the unique fingerprint spectrum that each gives. A high-energy beam of electrons bombards the molecules knocking out electrons and forming positive ions. The positive ion formed when the original molecule loses a single electron is called the parent molecular ion. Bombardment can cause the parent molecule to fragment; it loses an electron to form a smaller positive ion and a uncharged free radical. Further fragmentation of these fragments produces a range of positive ions that are recorded and measured by the detector. The most abundant ion formed is called the base peak and is assigned a relative abundance of 100%. Amounts of all other fragments are measured relative to the base peak.

Procedure

Each of three samples is injected in turn into the evacuated reaction chamber of the mass spectrometer. The fragmentation spectra produced are shown in Figures 37.1–37.3.

Questions

Questions 1–6 refer to Figure 37.1.

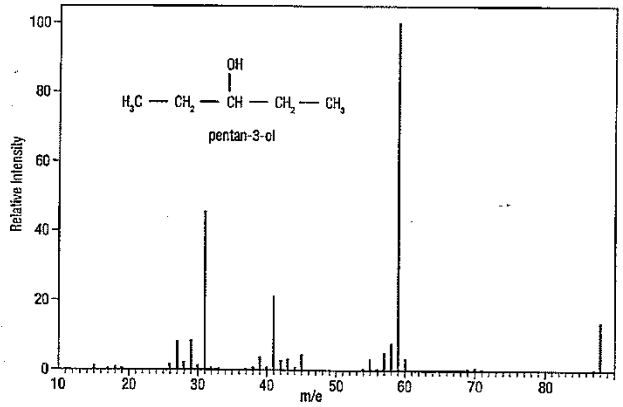


Figure 37.1 Mass spectrum and formula of pentan-3-ol

1 What is the mass to charge ratio, m/e, of the parent molecular ion of pentan-3-ol?
2 What is the mass of the ion that forms the base peak?
3 Draw an equation to represent the formation of this ion.
4 What is the mass of the uncharged fragment left when the base peak is formed? Does this fragment also form as an ion and appear on the mass spectrum?
5 The base peak ion can undergo a rearrangement to lose a molecule of water. Write an equation to represent the rearrangement. What is the m/e of the ion that results?
6 Complete Table 37.1 identifying possible structures that produce peaks at m/e as indicated.

Questions 7–9 refer to Figure 37.2.

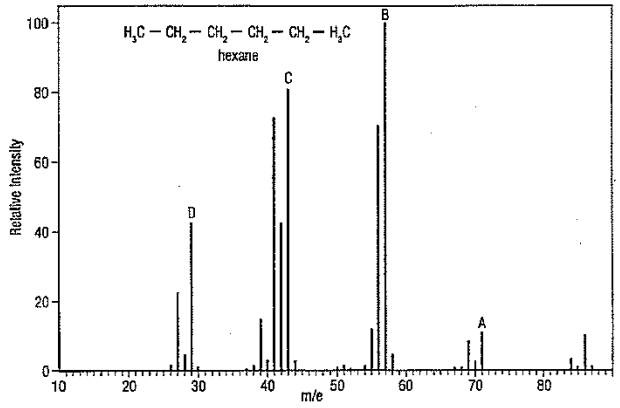


Figure 37.2 Mass spectrum and formula of hexane

7 What is the mass difference between the peaks marked by the letters A, B, C and D in the spectrum?
8 What fragment does this represent?
9 Write equations or draw a diagram to show the successive fragmentation from *m/e* 86, 71, 57, 43, 29, 15.

Questions 10 and 11 refer to Figure 37.3.

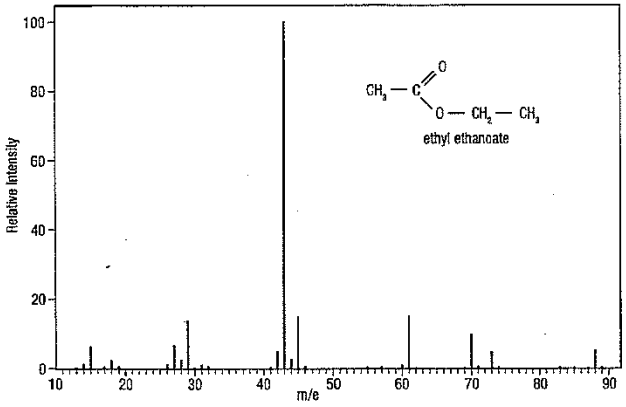


Figure 37.3 Mass spectrum and formula of ethyl ethanoate

10 Draw and complete Table 37.2 summarising the major peaks in the spectrum.
11 The peak at *m/e* 61 is formed after fragmentation of the parent molecular ion and then the rearrangement of two hydrogen atoms. Give the formula of the uncharged fragment remaining.

Table 37.1

m/e	Possible structure
e.g. 15	CH_3
29	
31	
41	
59	

Table 37.2

m/e	Possible structure
88	
45	
43	
29	

Spectroscopic Analysis – Data Table

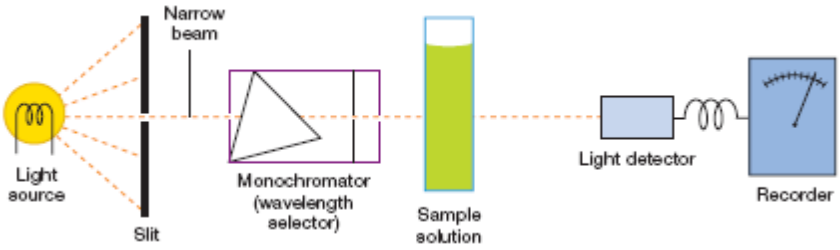
	Colorimetry	UV-visible Spectroscopy	Atomic Absorption Spectroscopy	Infrared	Nuclear Magnet Resonance
Samples able to be tested					
How are the samples treated?					
How is the wavelength of electromagnetic radiation determined?					
How is concentration determined? (The formation of calibration curves)					
How is absorbance measured?					
How is the instrument calibrated?					
Qualitative or Quantitative?					

Analytical Instruments – Data Table

Instrument	Principles of Use	Qualitative Measure	Quantitative Measure	Samples Tested
TLC	• Sample spotted on origin • Standards spotted on origin • Liquid solvent passes up through the solid stationary phase • Separation due to solubility in mobile phase and level of adsorption to stationary phase	R_f	none	Water soluble and less polar compounds
HPLC	• Sample injected into column • High pressure is applied • Liquid solvent (the eluent) carries sample through the solid stationary phase • Separation due to solubility in mobile phase and level of adsorption to stationary phase	R_t	Peak area on chromatogram	Organic compounds that are too big to vaporise easily or those that decompose on heating
GLC	• Sample injected into column at high temperature and is vaporised • Carrier gas (inert such as nitrogen) carries sample through the liquid stationary phase (high boiling point hydrocarbon or ester on a solid support) • Separation due to solubility in mobile phase and level of adsorption to stationary phase	R_t (generally smaller molecules pass through most quickly)	Peak are on chromatogram	Gaseous samples or those that are easily vaporised (molecular masses< 300)
Colorimeter	• Light passed through a coloured filter (colour selected that is absorbed well by the sample) • Detector measures the amount of light absorbed • Standards run first to create a calibration curve • Test sample has absorbance measured and this figure is compared to the calibration curve in order to determine the concentration		Concentration determined through reference to a calibration curve	Most metals as coloured compounds and a few anions as coloured compounds
UV/Vis	• Monochromator used to select a single wavelength (λ) of light (in the UV and visible part of the spectrum that is absorbed best by the test sample • Detector measures the amount of light absorbed • Standards run first to create a calibration curve • Test sample has absorbance measured and this figure is compared to the calibration curve in order to determine the concentration	Only by comparing absorption spectra	Concentration determined through reference to a calibration curve	Most metals as coloured compounds and a few anions as coloured compounds
AAS	• Cathode lamp emits light specific to the sample test metal • Sample is vaporised in a flame and atoms are left in the ground state • Light passes through sample and into a monochromator which selects only the wavelength of interest to be passed to the detector • Detector measures the amount of light absorbed • Standards run first to create a calibration curve • Test sample has absorbance measured and this figure is compared to the calibration curve in order to determine the concentration	Only the test metal will absorb the wavelengths of light being emitted by the excited metal atoms in the cathode lamp	Concentration determined through reference to a calibration curve	All metals and metalloids

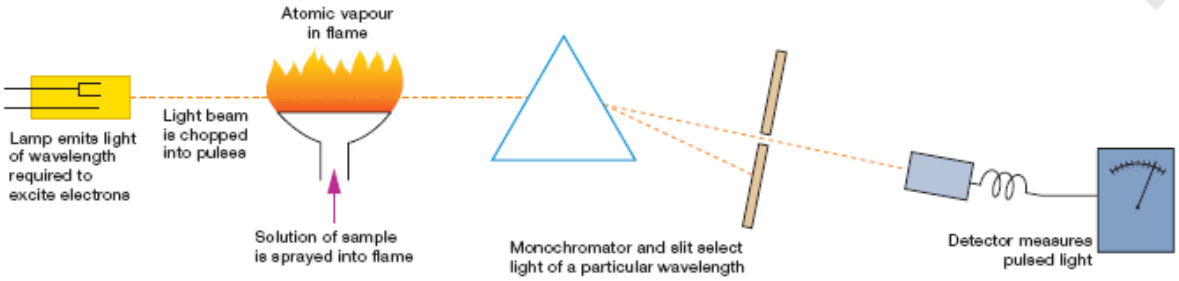
Analytical Instruments

Identify the following instruments and name two components that help you in your choice.



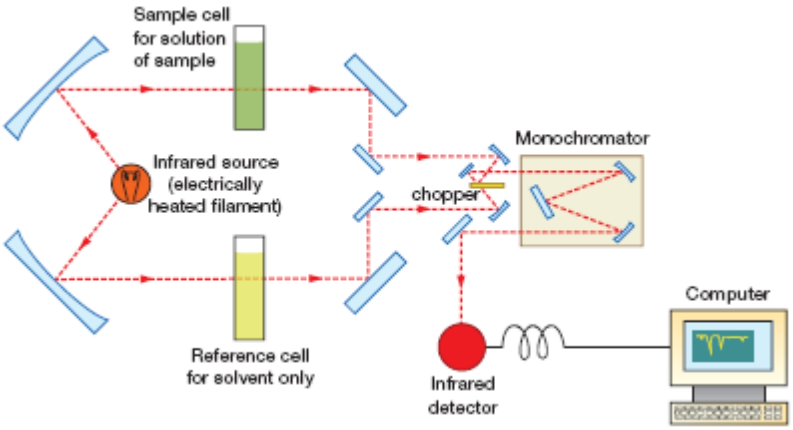
Instrument

Features



Instrument

Features



Instrument

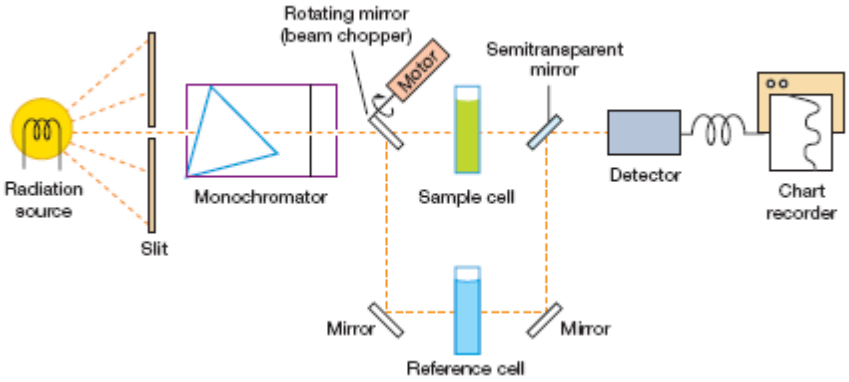
Features

Explain the role of the monochromators in analytical instruments.

_____

_____

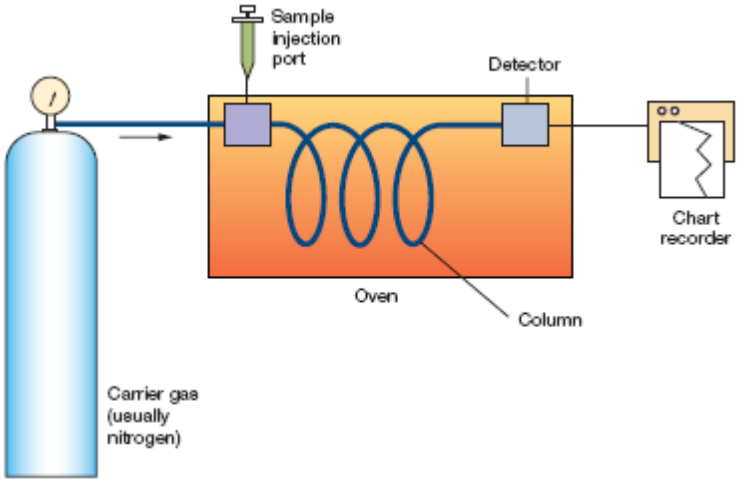
_____



Instrument

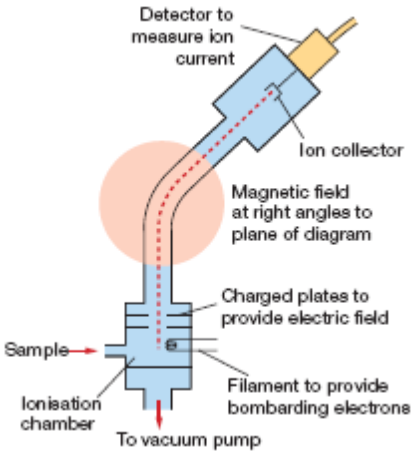
Features

Discuss the role of the reference cell.



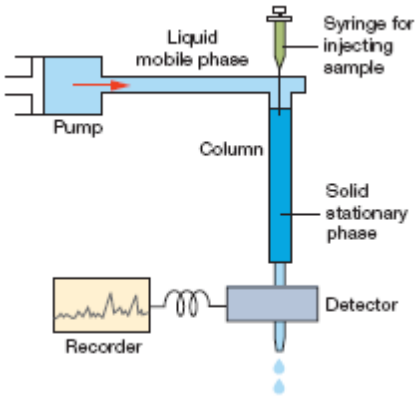
Instrument

Features



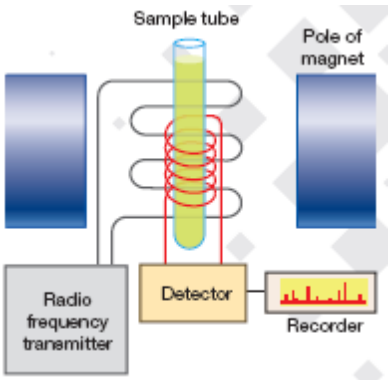
Instrument

Features



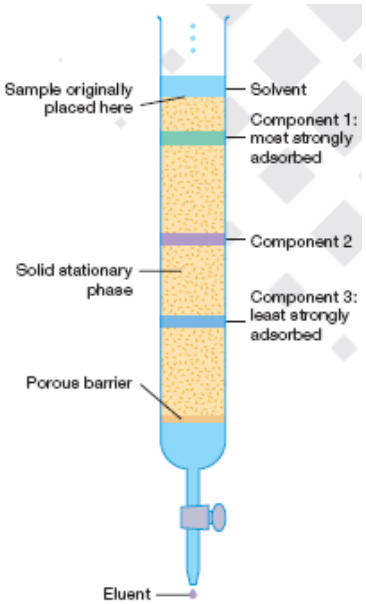
Instrument

Features



Instrument

Features



Instrument

Features

Chemical Analysis – Student Booklet

Outcome 1: Evaluate the suitability of techniques and instruments used in chemical analysis

Refer to Table 8.1 on p.120 and compare with this table below.

Technique	Typical Analytes	What the technique does and reveals
Gravimetric Analysis	H_2O, NaCl, Ag	• Precipitates dissolved ions • Determines the concentration of ions in consumer goods • Won't work for ions that do not precipitate: NH_4^+, CH_3COO^-, NO_3^-, Na^+, K^+
Mass Spectrometry	Any element or compound that can be volatilised	• Ionises and fragments molecules and separates them according to mass/charge ratios • Determines RIM & RAM of elements • Helps determines the structure of molecules • Molecules must be volatile without degrading
Volumetric Analysis	Acid/Base and Redox	• Uses standard solutions to determine the concentration of acid/base and redox reagents in mixtures eg. alcohol in wine • Many sources of experimental error eg. unclear end-points, uncertainties in instruments
TLC	Dyes, amino acids, Water soluble and less polar compounds	• Separates components in mixtures according to solubility in solvents and adsorption to stationary phase • Results are often not clear and well defined – is a simple, crude technique
GLC	Foods, drugs, biological samples	• Qualitative = Rt value • Quantitative = area under peak on chromatogram • Can only use gaseous samples or those that are easily vaporised (molecular masses< 300) • Samples that caramelise cannot be analysed
HPLC	Foods, drugs, biological samples	• Qualitative = Rt value • Quantitative = area under peak on chromatogram • Can only use gaseous samples or those that are easily vaporised (molecular masses< 300) • Samples that caramelise cannot be run
AES	Many metals: Ca, Na, Mg	• Qualitative method where emitted light is passed through a prism to produce a characteristic emission spectrum • Emission spectra are produced by electrons being excited between energy levels within an atom • All elements have a unique emission spectrum due their unique electron configurations
AAS	Most metals: Cu, Fe, Zn	• Determines the concentration of metals in mixtures • Standard solutions produce calibration curves to which unknown solutions are compared • Absorption of light specific to an element is due to electrons being excited between energy levels within the atom
UV-Visible	Low molecular mass organic chemicals such as asprin	• Determines the concentrations of organic molecules through the absorption of light in the UV-Visible part of the electromagnetic spectrum • Absorption wavelength is selected by scanning the molecules absorption across a range of wavelengths • Selected wavelength will be one where thre molecule of interest absorbs well and where other molecules in the mixture will not absorb strongly
IR	Organic molecules Quantitative for determining SO_2, HCN & CS_2 levels in the atmosphere	• Lower energy EMR causes changes in bonds which absorb at typical wavelengths • Identifies functional groups and reveals a lot about the structure of molecules • Quantitative when a selected wavelength is chosen and standards are run to produce a calibration curve
NMR	Organic molecules	• Magnetic fields and radiowaves cause energy splits in the nucleus of atoms • Reveals a lot about the structure of molecules by identifying C & H environments • No' of peaks = no' of H environments • Chemical shift identifies the type of H environment • Relative peak area = no' of protons in a particular environment • Peak splitting identifies the no' of protons neighbouring a H environment