

Mastering Chemistry

Book 8

Topic 15 Analytical Chemistry



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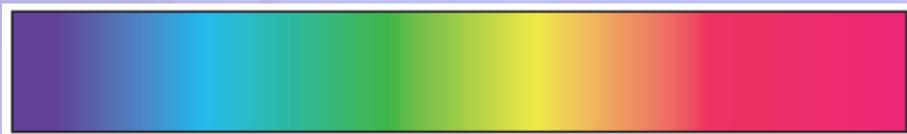


54.1 Instrumental analytical methods (p.122)

- ◆ Instrumental analytical methods rely on machines to carry out analyses of substances. These methods have become the principal means of obtaining information in diverse areas.
- ◆ Compared with traditional analytical methods such as volumetric analysis, instrumental analytical methods have several advantages, including
 - fast — instruments can carry out analyses quickly and they can run all the time;
 - increased level of accuracy;
 - increased level of sensitivity — instruments can analyse very small amounts of substances.
- ◆ The instruments are usually costly and require trained persons for operation.

 54.2 Colorimetry (p.123)

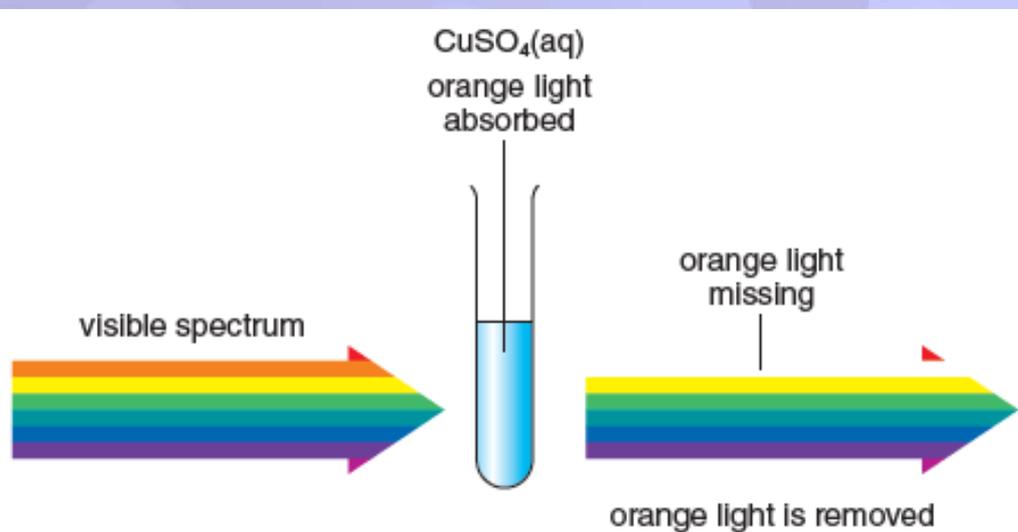
- ◆ The electromagnetic spectrum is the range of all possible electromagnetic radiations.
- ◆ The visible spectrum is the section of the electromagnetic spectrum that is visible to the human eye.
- ◆ White light is light made up of all the colours of the visible spectrum.
- ◆ Visible light has wavelengths ranging from 400–700 nanometres.



The visible spectrum which can be seen by the human eye

 54.2 Colorimetry (p.123)

- ◆ When white light passes through copper(II) sulphate solution, orange light is absorbed. This means that the light coming out contains all the colours of the spectrum except orange.
- ◆ The light appears blue which is the **complementary colour (互補色)** to orange.



Copper(II) sulphate solution absorbs orange light (The spectra in this diagram are for illustration only and are NOT real.)



54.2 Colorimetry (p.123)

- ◆ The colour of a substance that you see is white light minus the colour being absorbed by the substance.
- ◆ The colour you see is the complementary colour to the colour being absorbed.
- ◆ A colour wheel shows which pairs of colours are complementary (opposite each other in the colour wheel).



A simple colour wheel: complementary colours are opposite one another

 54.2 Colorimetry (p.123)

- ◆ Whilst the colour of a solution depends on the colour of light it absorbs, the **intensity** (強度) of its colour depends on the concentration of the solution.
- ◆ The more concentrated the solution, the more intense its colour, that is, the more light it absorbs.

Colorimetry is a technique for determining the concentration of a chemical species in solution based on its ability to absorb certain parts of the radiation of the visible spectrum.

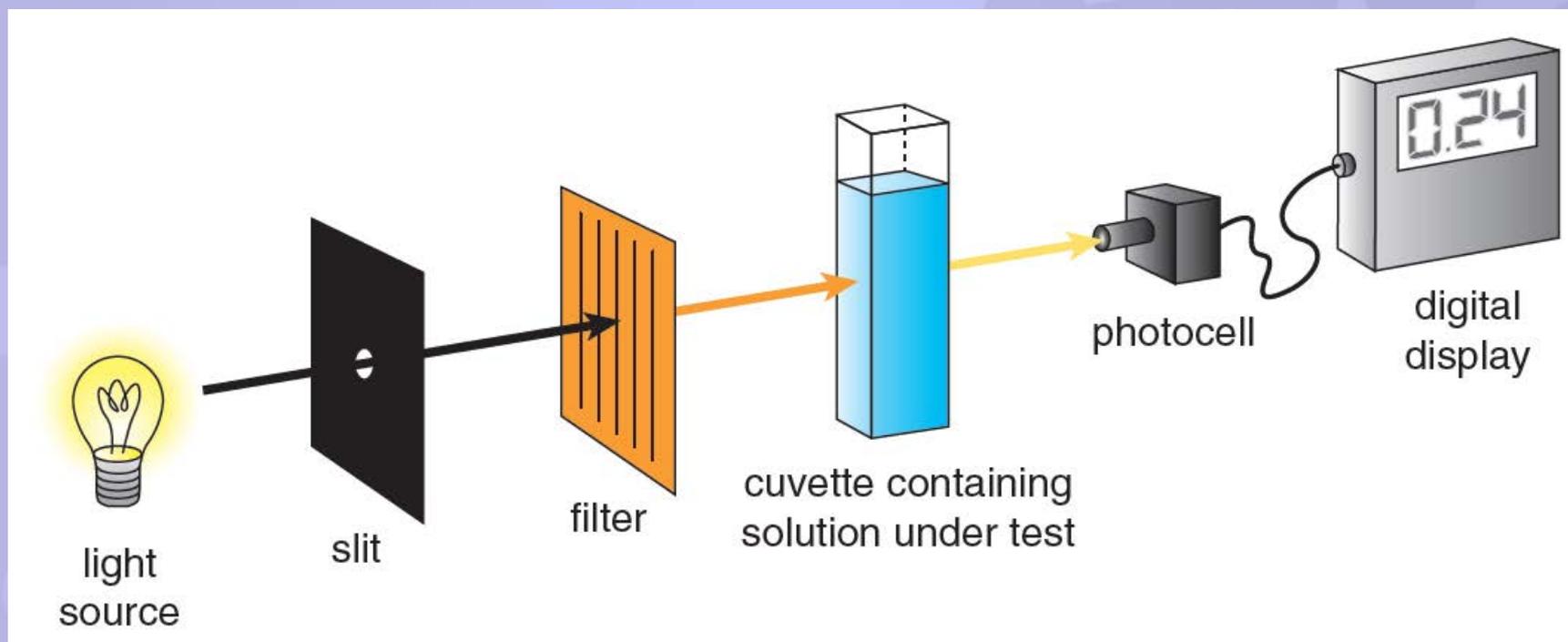
- ◆ The colorimetric determination is carried out by using a device called a **colorimeter** (比色計).





54.3 How a colorimeter works (p.125)

- ◆ The light from the light source is passed through a filter which changes the light to a specific colour. The incident light then passes into the solution under test in a cuvette.



Components of a colorimeter



54.3 How a colorimeter works (p.125)

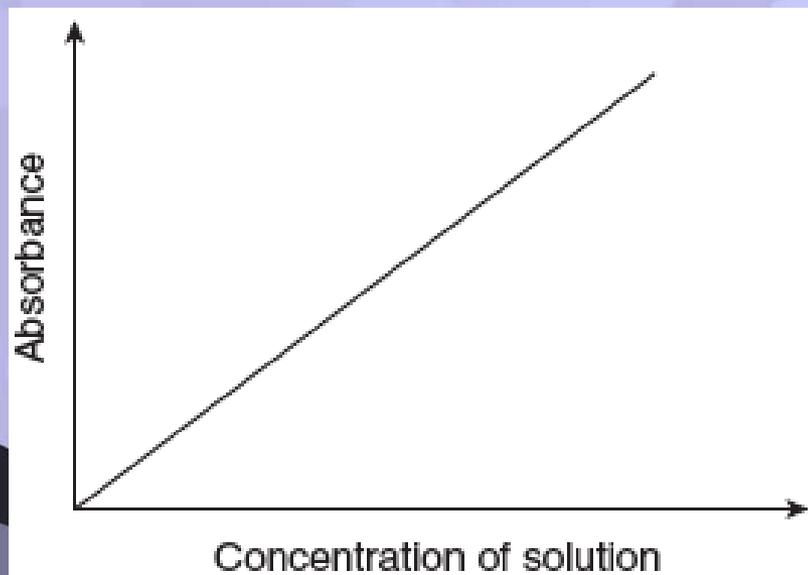
- ◆ The filter colour must correspond to the colour of light that is strongly absorbed by the solution under test, i.e. choose a filter of complementary colour to the colour of the solution.
- ◆ For example, a blue filter allows blue light to pass through. A blue solution is not absorbing blue light so a blue filter would be useless. An orange filter should be used as the blue solution absorbs orange light to a large extent.
- ◆ **Absorbance (吸光度)** (A) of the sample is determined by comparing the intensity of the incident light (I_o) to the intensity of light after it has passed through the sample (I_s) using the following equation:

$$A = \log \left(\frac{I_o}{I_s} \right)$$



54.3 How a colorimeter works (p.125)

- ◆ If the absorbances of a series of standard solutions containing a solute are measured and plotted against their corresponding concentrations, a directly proportional line is obtained. This is known as a **calibration curve** (校準曲線).
- ◆ Use this graph to determine the concentration of an unknown sample solution from its absorbance.



A calibration curve plotting the absorbances of a series of standard solutions against their corresponding concentrations



54.4 Applications of colorimetry (p.126)

- ◆ An aqueous solution of potassium permanganate has a purple colour and its concentration can be determined by using colorimetry.
- ◆ Colorimetry can be used to follow the progress of the reaction when acidified aqueous solution of potassium permanganate oxidises an aqueous solution of sodium ethanedioate.
- ◆ Colorimetry can be used to determine the concentrations of plant nutrients such as ammonia and phosphorus in soil.
- ◆ Colorimetry is used in industries like colour printing, textile manufacturing and paint manufacturing. It is also widely used in food and drug industries.



Determining the content of food dye in soft drinks Ref.



54.4 Applications of colorimetry (p.126)

Determining the amount of food dye present in a packaged soft drink

- ◆ Food dyes are often added into packaged food products to give the product a more appealing colour to attract customers.
- ◆ For example, Sunset Yellow is a commonly used food dye that can be found in a number of commercial products.
- ◆ Sunset Yellow gives the product an orange shade.

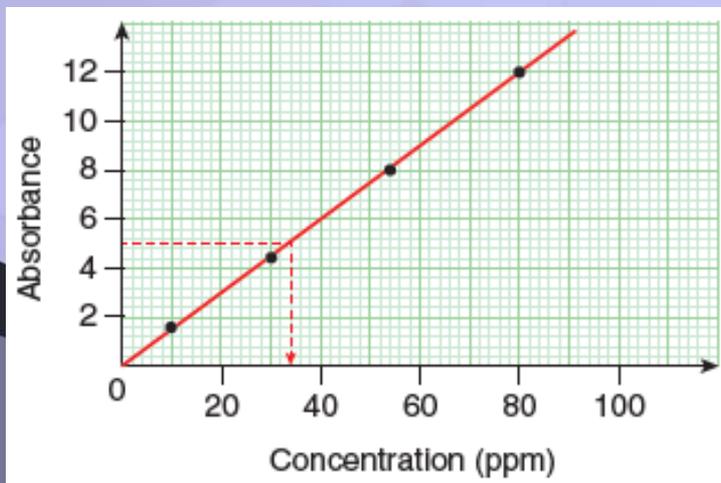


Sunset Yellow



54.4 Applications of colorimetry (p.126)

- ◆ A LED based colorimeter using a green LED as light source, and a stock solution of Sunset Yellow (concentration 100 ppm) are provided to determine the amount of Sunset Yellow in a given packaged soft drink sample.
- ◆ Prepare a series of standard solutions of Sunset Yellow of different concentrations. The absorbances of these standard solutions are determined for plotting an absorbance-concentration calibration curve.



An absorbance-concentration calibration curve of standard solutions of Sunset Yellow



54.4 Applications of colorimetry (p.126)

Suppose 5.00 cm^3 of a soft drink sample is diluted to 10.00 cm^3 . The absorbance of the diluted sample is found to be 5.0. From the calibration curve in the previous page, you can see that the concentration of Sunset Yellow in the diluted sample is 34 ppm. The soft drink sample is diluted from 5.00 cm^3 to 10.00 cm^3 .
 \therefore concentration of Sunset Yellow in the soft drink sample

$$= 34 \text{ ppm} \times \frac{10.00 \text{ cm}^3}{5.00 \text{ cm}^3}$$

$$= 68 \text{ ppm}$$

$$= 68 \times 10^{-3} \text{ g dm}^{-3}$$

$$= \frac{68 \times 10^{-3} \text{ g dm}^{-3}}{452.4 \text{ g mol}^{-1}}$$

$$= 1.5 \times 10^{-4} \text{ mol dm}^{-3}$$



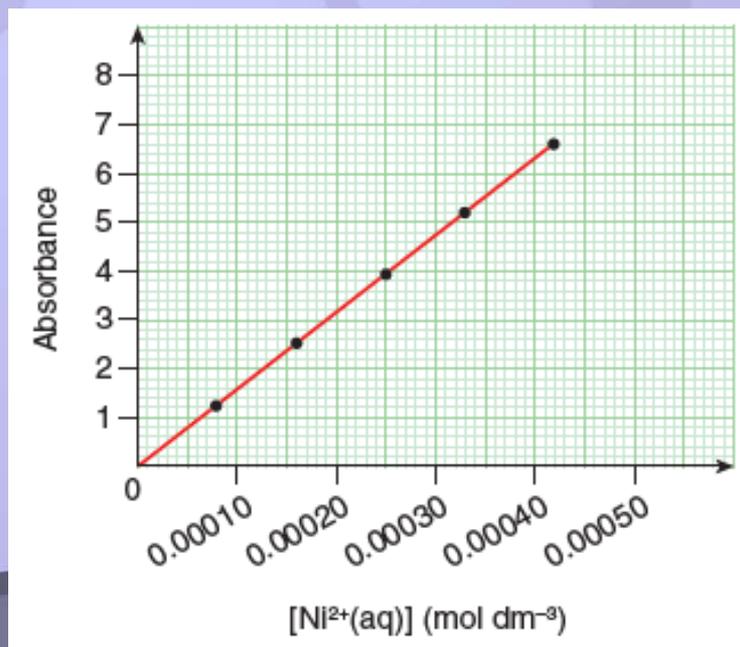
54.4 Applications of colorimetry (p.126)

Practice 54.1

- 1 Instrumental methods of analysis linked to computers can be used to identify chemicals. Describe TWO advantages of using instrumental methods of analysis.
- 2 Various standard $\text{Ni}^{2+}(\text{aq})$ solutions were first prepared, and then the absorbances of these solutions were measured with a colorimeter installed with an appropriate LED light source. The calibration curve below shows the variation of absorbance with the concentration of $\text{Ni}^{2+}(\text{aq})$ ion.

1 Any two of the following:

- Fast / quick
- Can detect small amounts of samples / sensitive
- Accurate
- Ease of automation
- Sample not used up
- Reliable / efficient
- Can be left to run / continuous analysis





54.4 Applications of colorimetry (p.126)

Practice 54.1 (continued)

a) Which of the following LEDs should be used in this experiment? Explain your choice.

LED number	1	2	3	4	5	6
Colour of light emitted	red	orange	yellow	green	cyan	blue

b) With reference to the calibration curve, state the relationship between absorbance and $[\text{Ni}^{2+}(\text{aq})]$.

c) 20.0 cm^3 of a $\text{Ni}^{2+}(\text{aq})$ solution X was diluted to a total volume of 100.0 cm^3 . The absorbance of the diluted solution was measured as 3.0 by the colorimeter. Calculate the concentration of $\text{Ni}^{2+}(\text{aq})$ in X.

a) LED number 1

The green $\text{Ni}^{2+}(\text{aq})$ solution absorbs red light to a large extent.

b) The absorbance is directly proportional to the concentration of $\text{Ni}^{2+}(\text{aq})$.

c) Absorbance = 3.0, $[\text{Ni}^{2+}(\text{aq})]$ found from the graph = $0.00019 \text{ mol dm}^{-3}$

Solution X was diluted 5 times.

Concentration of $\text{Ni}^{2+}(\text{aq})$ in X = $5 \times 0.00019 \text{ mol dm}^{-3}$
 = $9.5 \times 10^{-4} \text{ mol dm}^{-3}$



54.5 Infrared spectroscopy (p.129)

- ◆ Spectroscopy refers to a wide array of different techniques that employ electromagnetic radiation to obtain data on the structure and properties of matter.
- ◆ The range of techniques available covers many regions of the electromagnetic spectrum of radiation — including the infrared, visible and ultraviolet regions.
- ◆ Infrared spectroscopy (or IR spectroscopy) is an analytical technique used to identify functional groups in organic molecules.



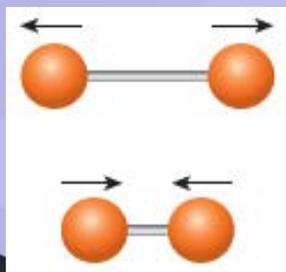
Vibrations in the CO₂ molecule [Ref.](#)



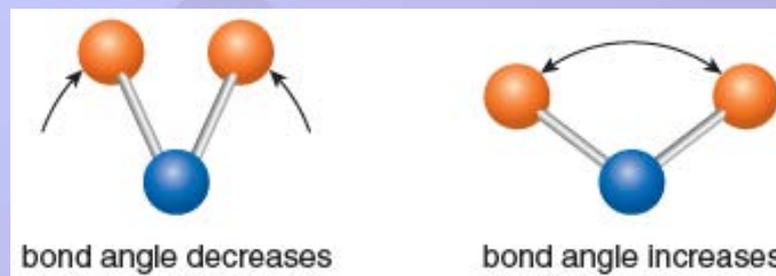
54.5 Infrared spectroscopy (p.129)

How infrared spectroscopy works

- ◆ Atoms in molecules are joined by covalent bonds. These bonds possess energy and vibrate naturally.
- ◆ One type of vibration, a stretch, is a rhythmic movement along the line between the atoms so that the distance between the two atomic centres increases and decreases.
- ◆ The second type of vibration, a bend, results in a change in bond angle.



A bond in a molecule can stretch so that the distance between the atomic centres changes



bond angle decreases

bond angle increases

Bonds in a molecule can bend, causing the bond angle to change



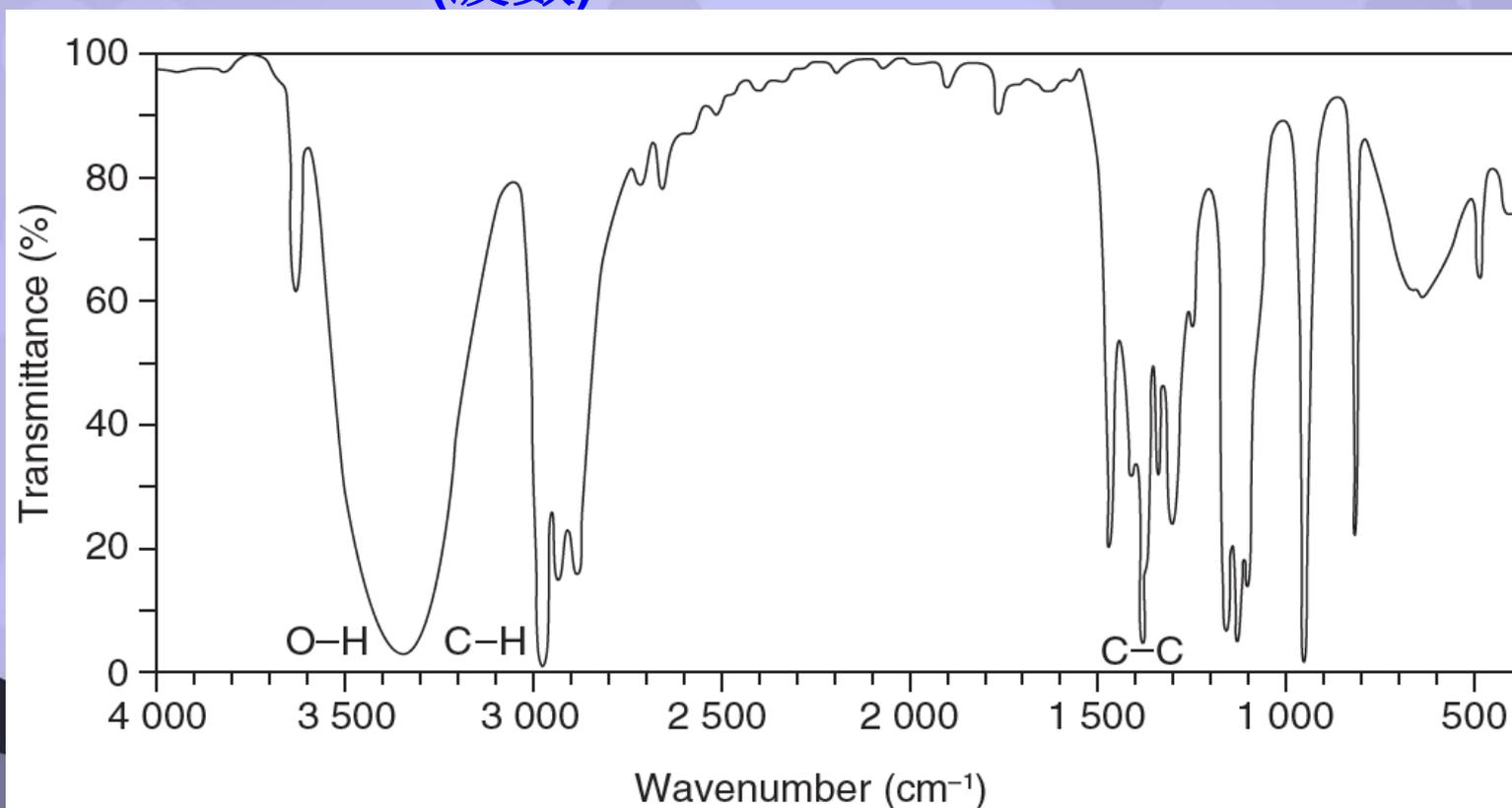
54.5 Infrared spectroscopy (p.129)

- ◆ Stronger bonds vibrate faster (at higher frequency) and heavier atoms make the bond vibrate more slowly (at lower frequency).
- ◆ These frequencies all lie within the infrared region of the electromagnetic spectrum of radiation.
- ◆ Any particular bond can only absorb radiation that has the same frequency as the natural frequency of the bond.
- ◆ An infrared spectrometer analyses a compound by passing infrared radiation through the sample and measuring the absorptions made by each type of bond in the compound. This produces an infrared spectrum.



54.6 What does an infrared spectrum look like? (p.131)

- The figure below shows the infrared spectrum of propan-2-ol. The spectrum is a plot of **transmittance** (透光率) against **wavenumber** (波數).





54.6 What does an infrared spectrum look like?

(p.131)

Axes

- ◆ The vertical axis is labelled transmittance, shown as a percentage from 0 to 100. A value of 100% transmittance means that 100% of the radiation is transmitted and none is absorbed.
- ◆ The horizontal axis is labelled wavenumber. The frequency values are very large, so chemists use a more convenient scale, the wavenumber.
- ◆ The wavenumber is equal to the number of waves per centimetre. It is quoted in the unit cm^{-1} . Wavenumber (symbol: $\tilde{\nu}$) and wavelength (symbol: λ) are related by the equation:
$$\tilde{\nu} \text{ (in cm}^{-1}\text{)} = \frac{1}{\lambda \text{ (in cm)}}$$
- ◆ The wavenumber is directly proportional to the frequency of the radiation.



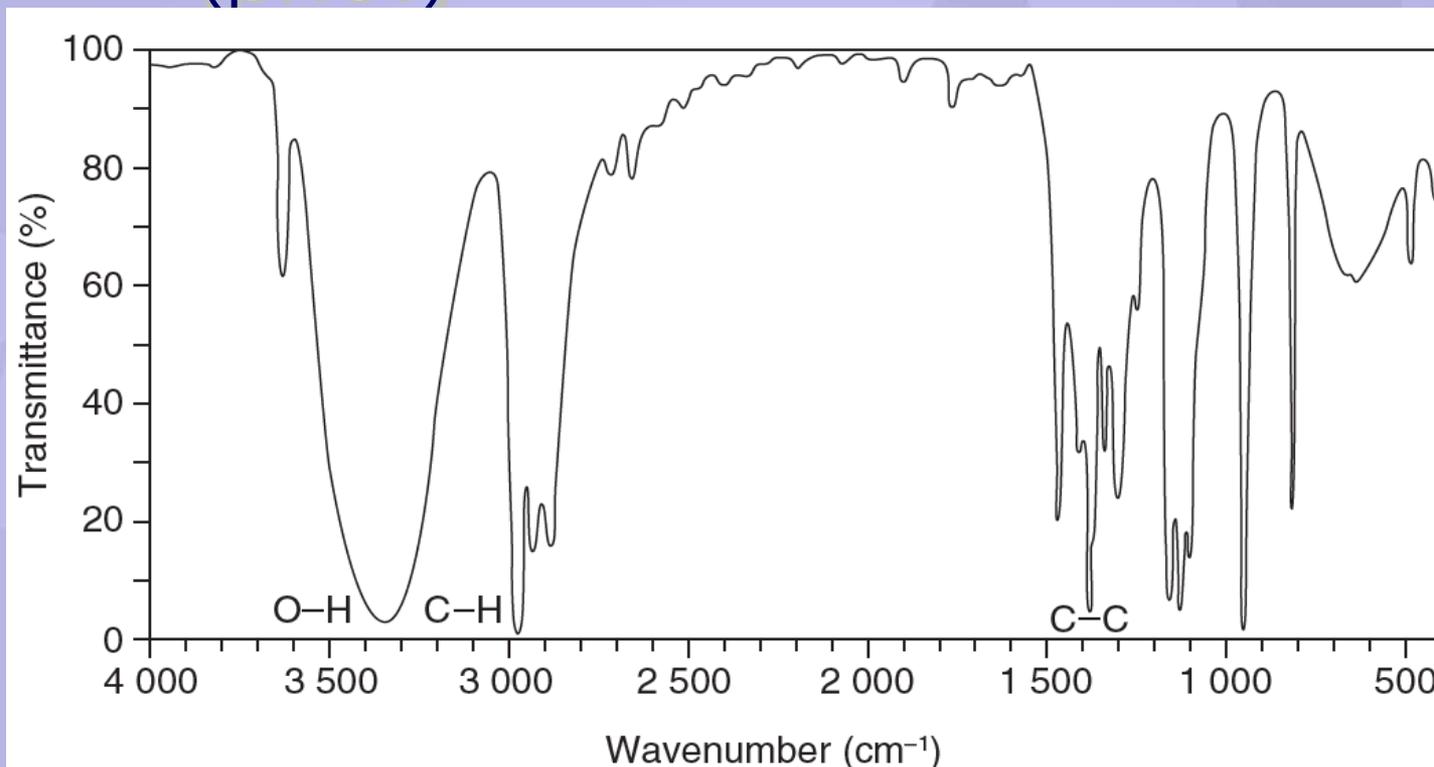
54.6 What does an infrared spectrum look like? (p.131)

Absorption peaks

- ◆ Much of the spectrum consists of an almost horizontal line close to 100%, but at specific wavenumbers there are dips. These are referred to as absorption peaks.
- ◆ The actual transmittance value of an absorption is not very important, but its intensity is.
- ◆ Weak intensities refer to high transmittance values, and strong intensities refer to low transmittance values.



54.6 What does an infrared spectrum look like? (p.131)



- the broad absorption peak at around 3 330 cm⁻¹ corresponds to O–H stretching;
- the absorption peak at 2 970 cm⁻¹ corresponds to C–H stretching;
- the absorption peak at 1 380 cm⁻¹ corresponds to C–C stretching.



54.7 Characteristic absorption wavenumber ranges for different bonds (p.133)

- ◆ Chemists have found that it is possible to correlate absorptions in the region $4\,000\text{--}1\,500\text{ cm}^{-1}$ with the stretching vibrations of particular bonds.
- ◆ Infrared spectra give valuable clues about the presence of functional groups in organic molecules.
- ◆ The precise position of an absorption depends on the environment of the bond in the molecule, so the wavenumber is only quoted as a range where the absorptions are expected to arise.



54.7 Characteristic absorption wavenumber ranges for different bonds (p.133)

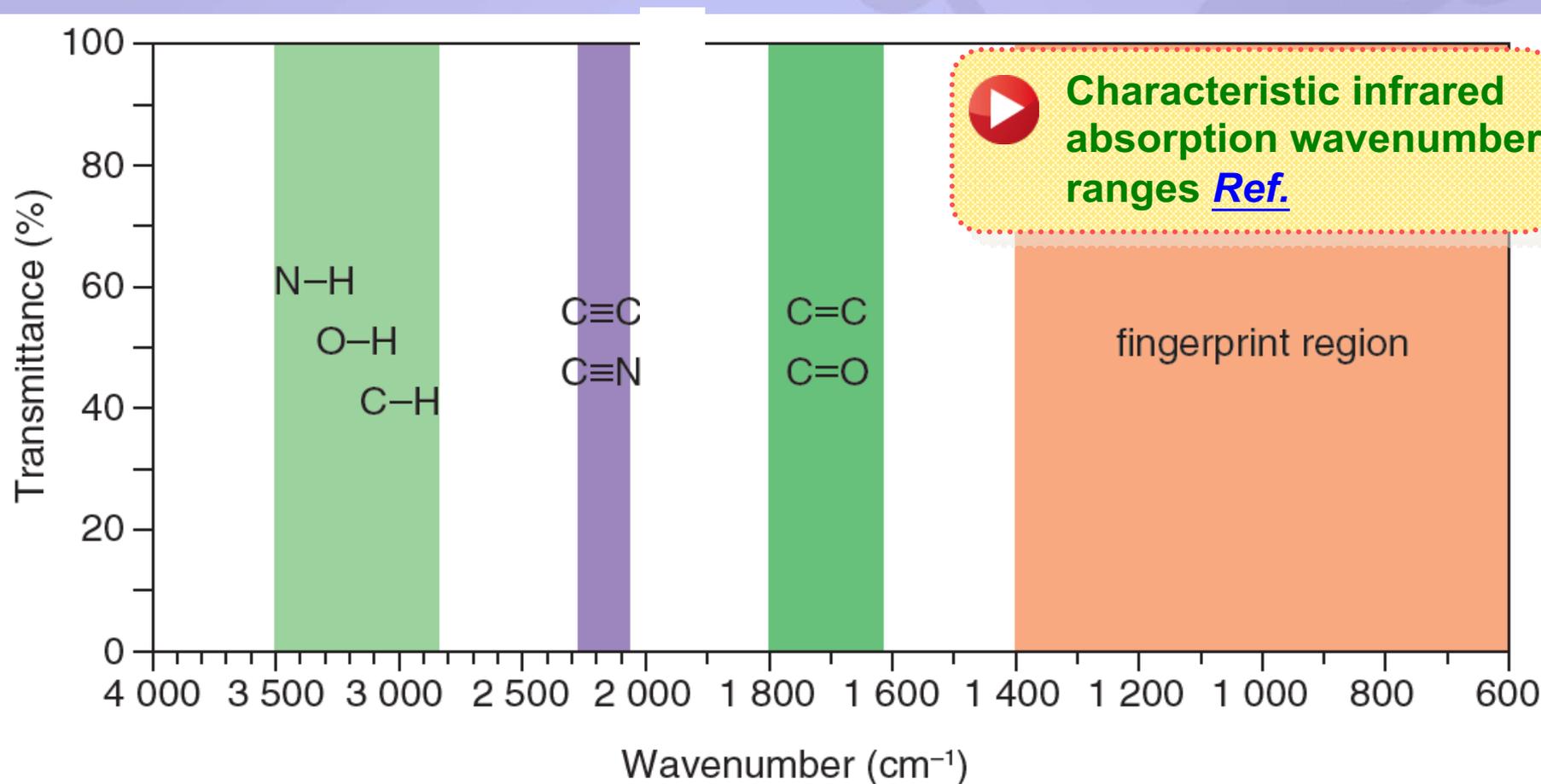
- The characteristic infrared absorption wavenumber ranges for some covalent bonds (stretching mode of vibration).

Bond	Compound type	Wavenumber range (cm ⁻¹)	Intensity
C=C	alkenes	1 610–1 680	medium
C=O	aldehydes, ketones, carboxylic acids and derivatives	1 680–1 800	strong
C≡C	alkynes	2 070–2 250	medium to weak
C≡N	nitriles	2 200–2 280	medium
O–H	acids (hydrogen-bonded)	2 500–3 300	strong, very broad
C–H	alkanes, alkenes, arenes	2 840–3 095	medium
O–H	alcohols, phenols (hydrogen-bonded)	3 230–3 670	strong, broad
N–H	amines	3 350–3 500	medium, broad



54.7 Characteristic absorption wavenumber ranges for different bonds (p.133)

- It is helpful to divide a infrared spectrum into four regions.





54.7 Characteristic absorption wavenumber ranges for different bonds (p.133)

- ◆ The absence of absorption peaks at certain characteristic wavenumber ranges provides important information as well.
- ◆ The information can be used to deduce that certain bonds (or functional groups) do not exist in the molecule of the sample being studied.

Identification of a carbon compound

- ◆ The area of an infrared spectrum below about $1\ 500\ \text{cm}^{-1}$ usually has many peaks caused by complex vibrations of the whole molecule.



54.7 Characteristic absorption wavenumber ranges for different bonds (p.133)

- ◆ This shape is unique for any particular substance. It can be used to identify the compound, just as people can be identified by their fingerprints. It is therefore called the **fingerprint region** (指紋區).
- ◆ Chemists can use a computer to match the fingerprint region of a sample with those in a database of compounds. An exact match confirms the identification of the sample.



54.7 Characteristic absorption wavenumber ranges for different bonds (p.133)

Test of purity

- ◆ The infrared spectrum of a pure compound should match that in the database. Any stray peaks will be due to impurities.
- ◆ For example, a peak at around 1700 cm^{-1} in the spectrum of an alcohol would probably be due to a carbonyl or carboxylic acid (and its derivatives) impurity.

There are two main uses for infrared spectra:

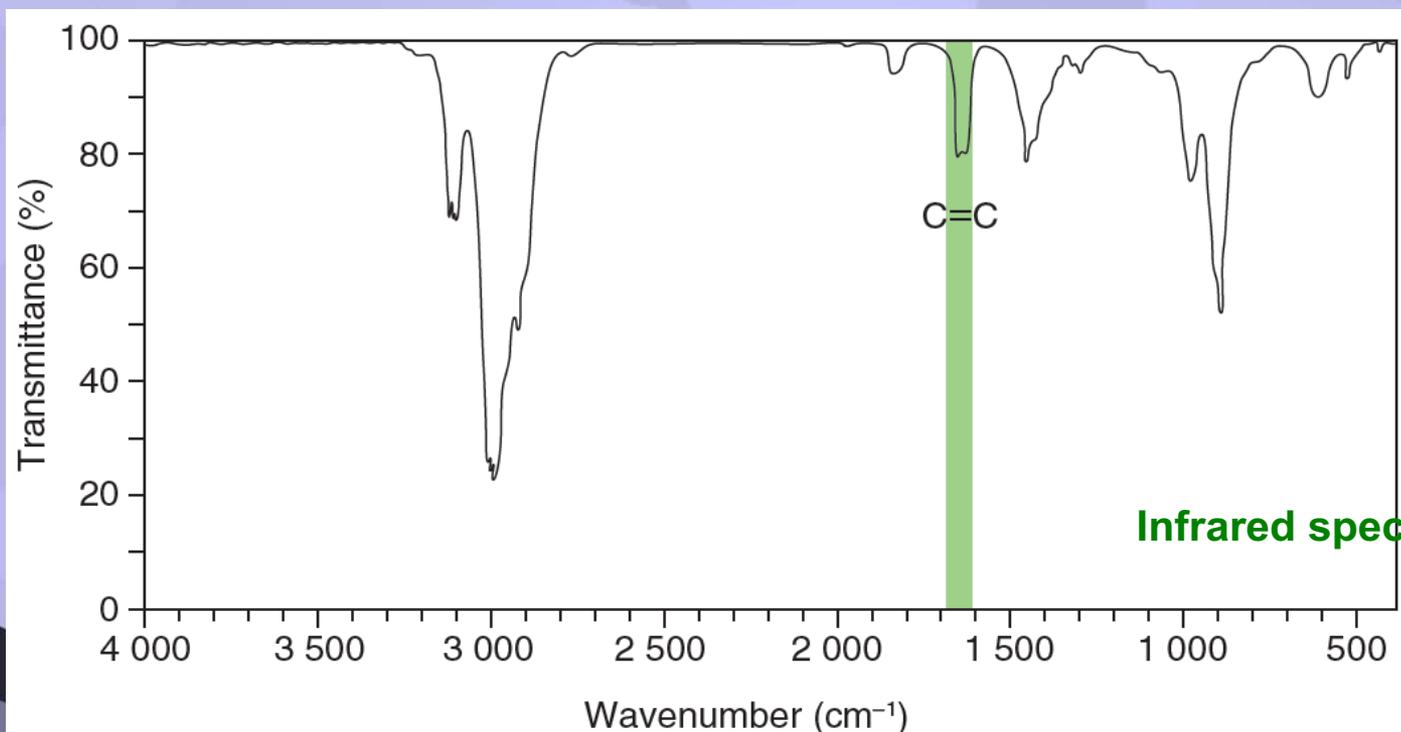
- to identify the functional groups present in molecules of carbon compounds;
- to identify carbon compounds (since each compound has a unique infrared spectrum).



54.8 Interpreting infrared spectra (p.135)

Infrared spectrum of an alkene

- The infrared spectrum of an alkene has an absorption peak within the range $1\ 610\text{--}1\ 680\ \text{cm}^{-1}$ which corresponds to the C=C bond.



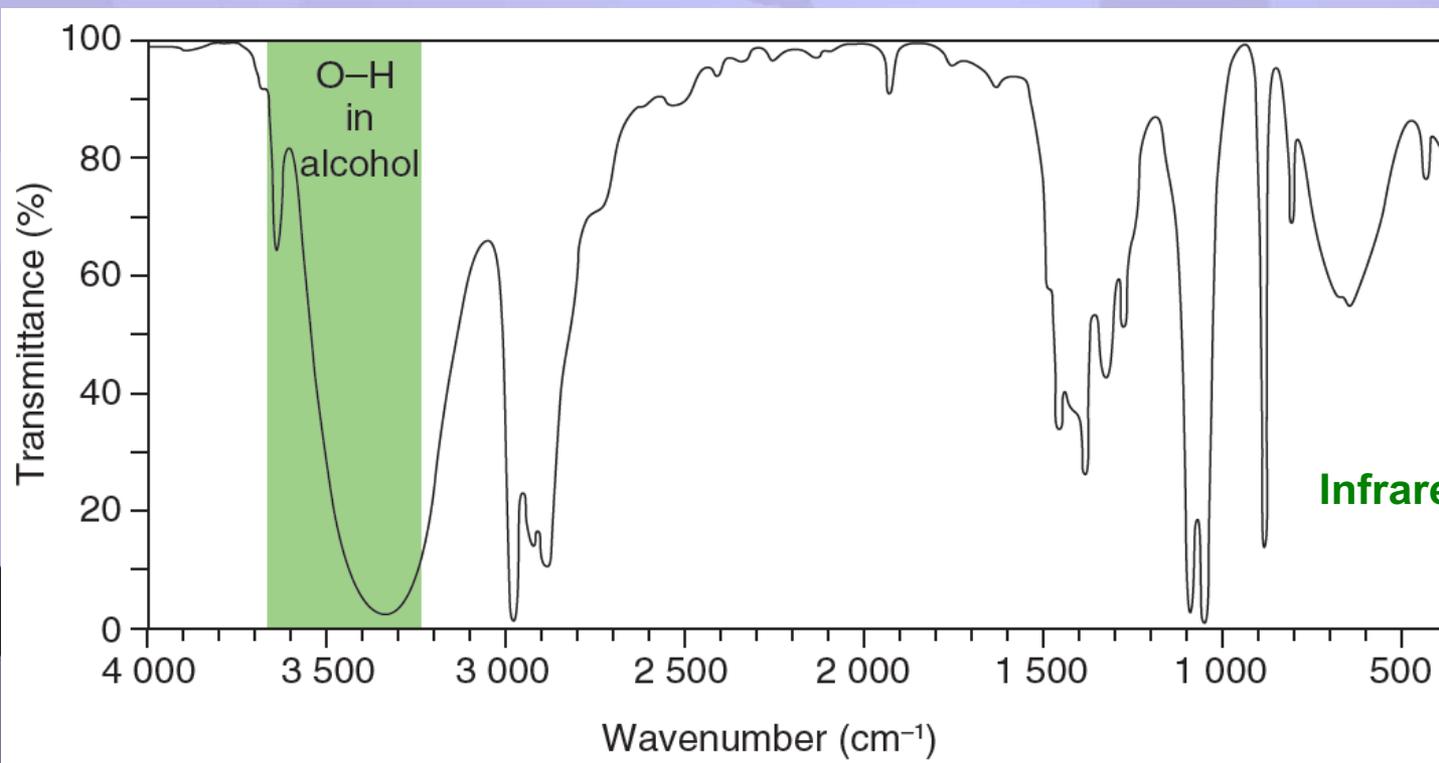
Infrared spectrum of but-1-ene



54.8 Interpreting infrared spectra (p.135)

Infrared spectrum of an alcohol

- The infrared spectrum of an alcohol has a broad absorption peak within the range $3\ 230\text{--}3\ 670\ \text{cm}^{-1}$ which corresponds to the O–H bond in the alcohol.



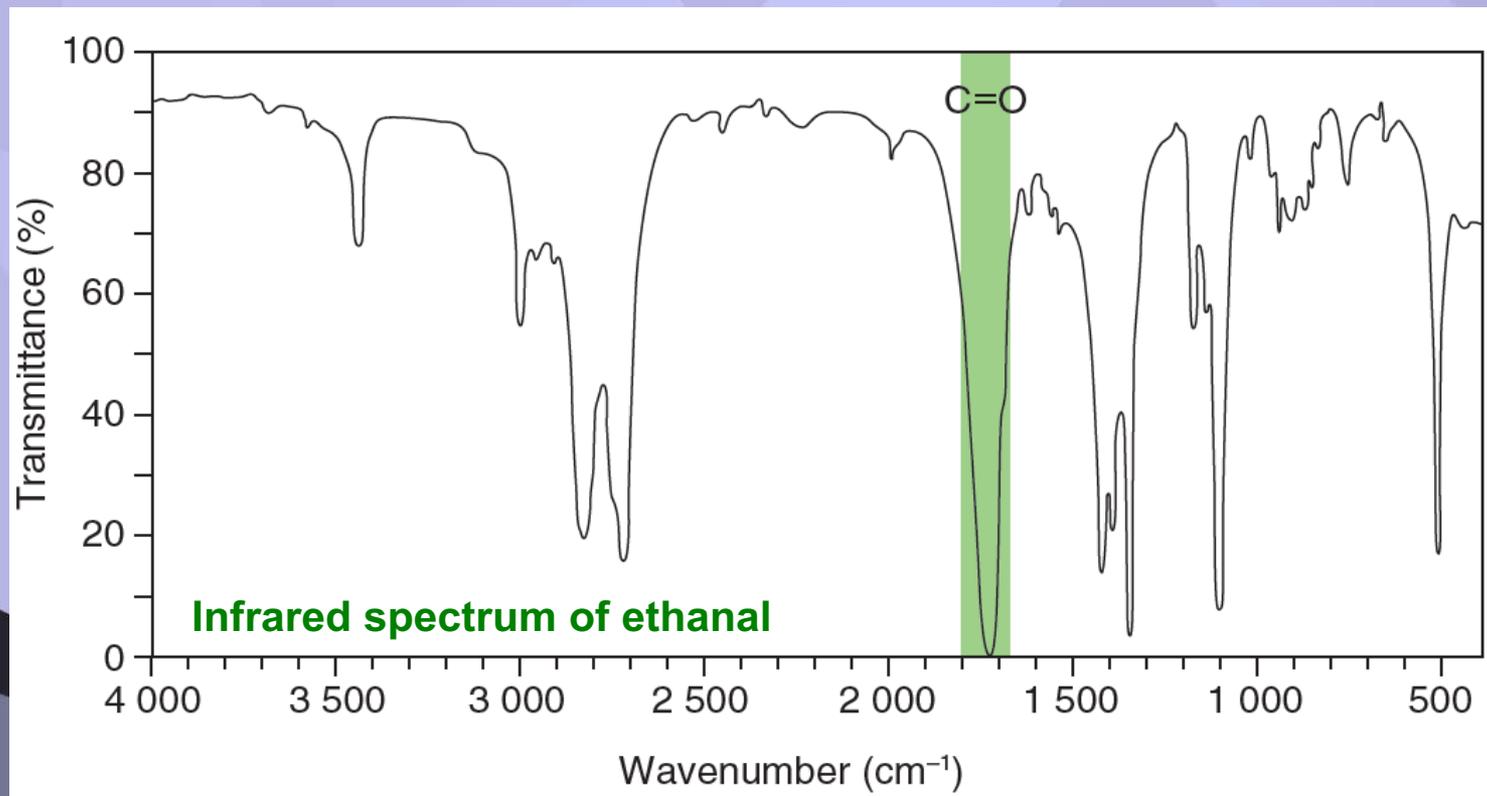
Infrared spectrum of ethanol



54.8 Interpreting infrared spectra (p.135)

Infrared spectrum of an aldehyde or ketone

- ◆ The infrared spectrum of an aldehyde or ketone has a strong absorption peak within the range $1\ 680\text{--}1\ 800\ \text{cm}^{-1}$ which corresponds to the C=O bond.





54.8 Interpreting infrared spectra (p.135)

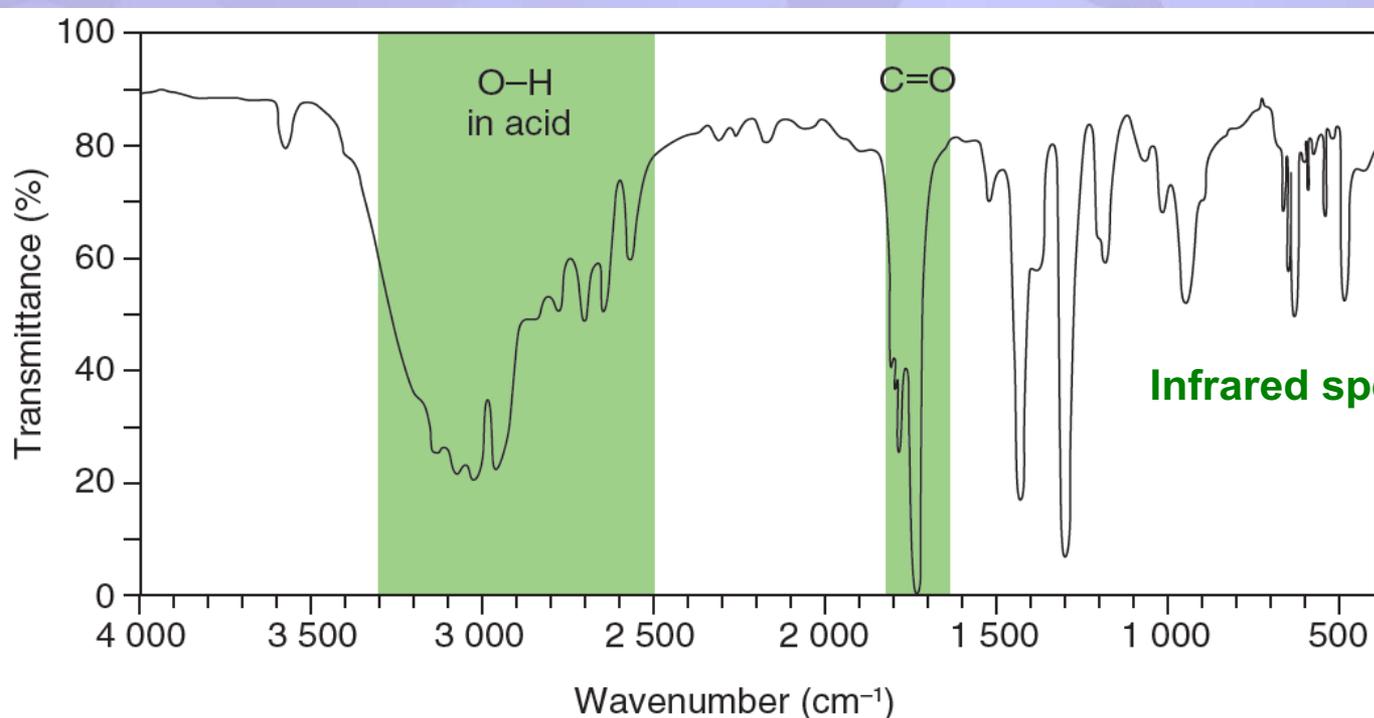
- ◆ The spectrum of an aldehyde or a ketone will have a peak corresponding to the C=O, but no peak corresponding to an O-H bond.



54.8 Interpreting infrared spectra (p.135)

Infrared spectrum of a carboxylic acid

- ◆ The infrared spectrum of a carboxylic acid has absorption peaks due to:
 - the C=O bond (in the region 1 680–1 800 cm^{-1});
 - the O–H bond, which has a very broad absorption peak (in the region 2 500–3 300 cm^{-1}).

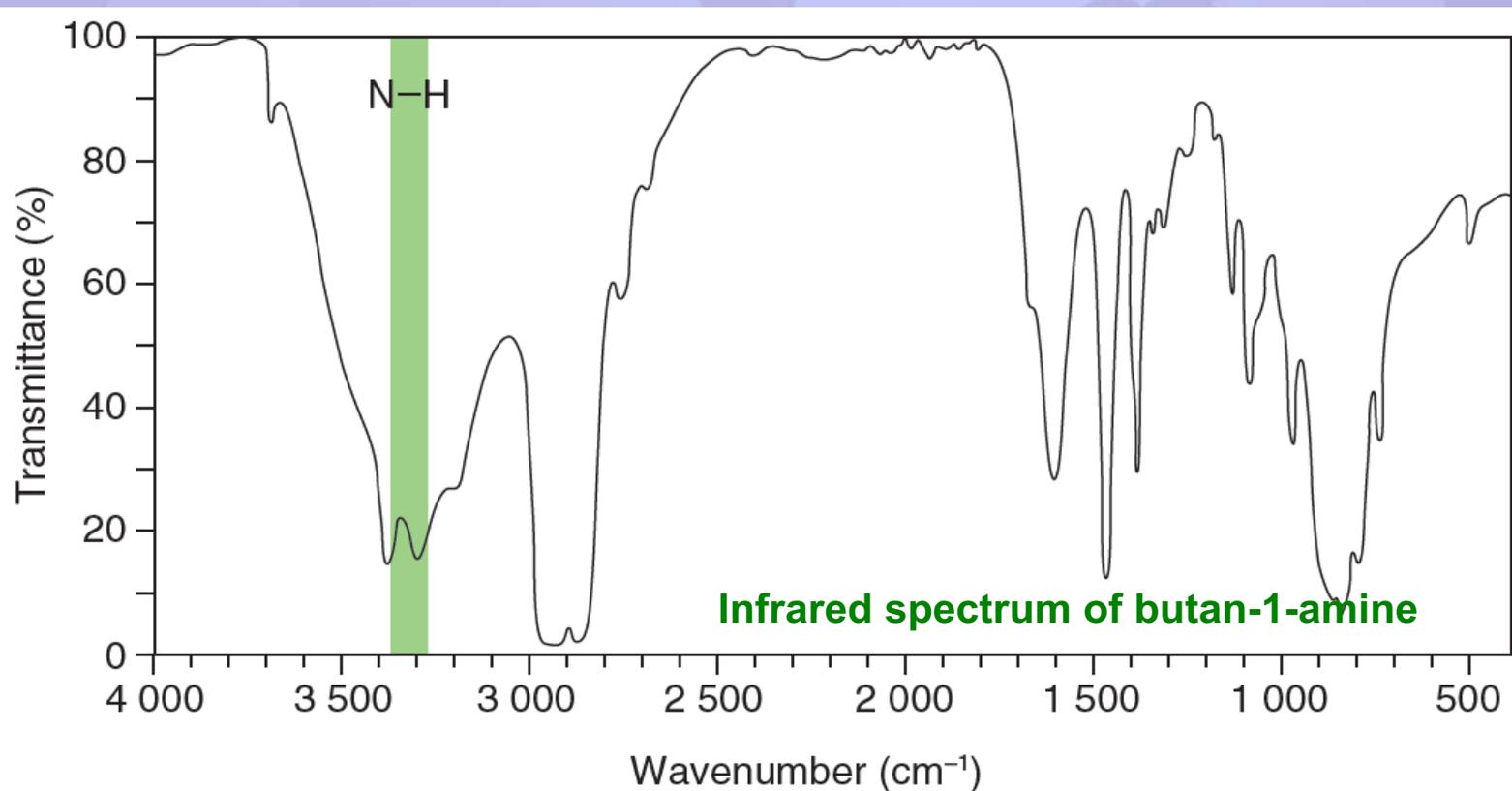




54.8 Interpreting infrared spectra (p.135)

Infrared spectrum of an amine

- The infrared spectrum of an amine has an absorption peak within the range $3\,350\text{--}3\,500\text{ cm}^{-1}$ which corresponds to the N–H bond.





54.9 Applications of infrared spectroscopy (p.138)

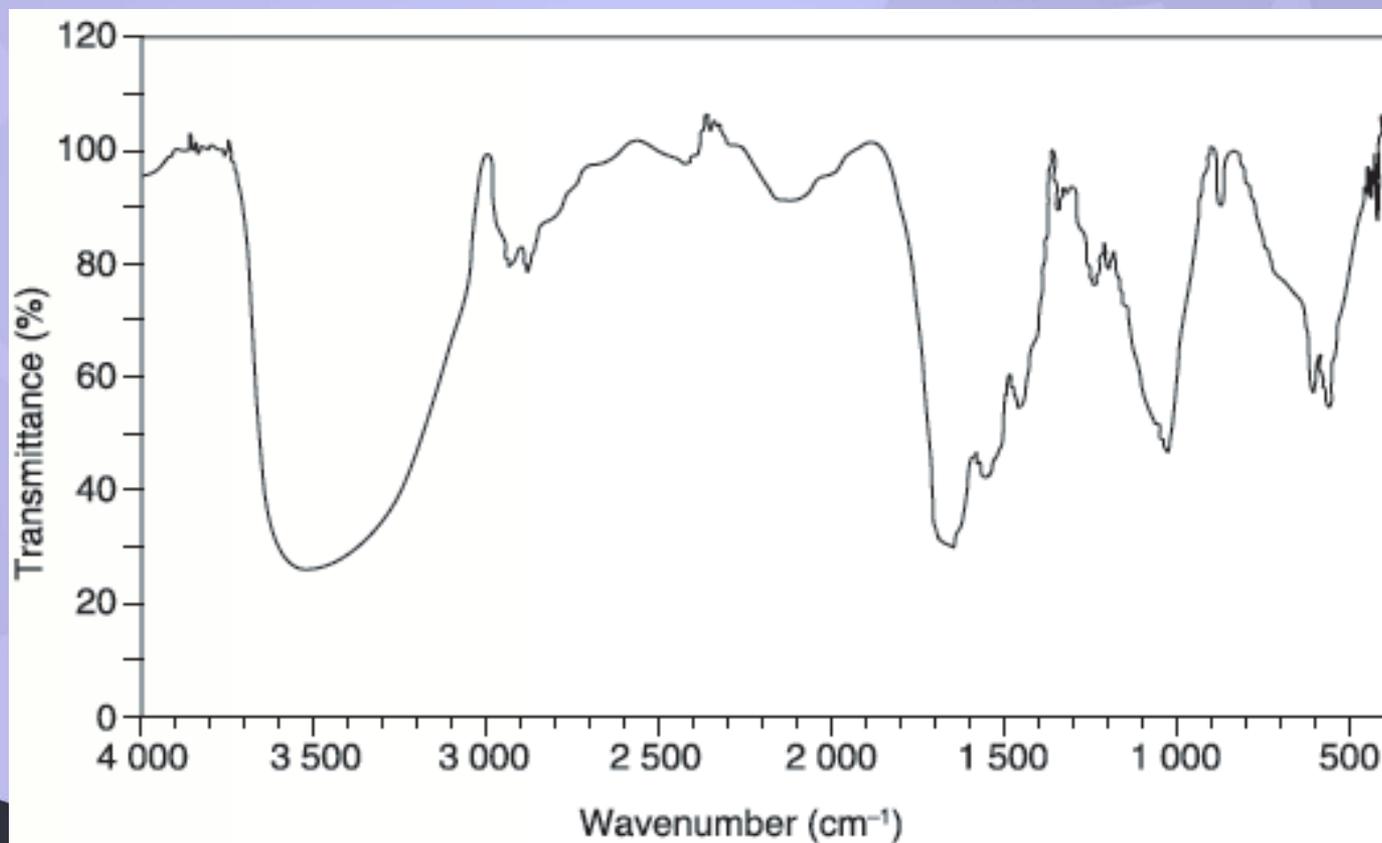
- ◆ Infrared spectroscopy is used extensively in forensic chemistry, for example, to analyse paint fragments from vehicles in hit-and-run offences. Other uses that rely on the technique include
 - monitoring the degree of unsaturation in polymers;
 - quality control in perfume manufacture;
 - testing the breath of suspected drunken drivers for ethanol;
 - routine checking of the composition of a medication to ensure that it is safe and effective.



54.9 Applications of infrared spectroscopy (p.138)

Q (Example 54.1)

The infrared spectrum of chitin is shown below.

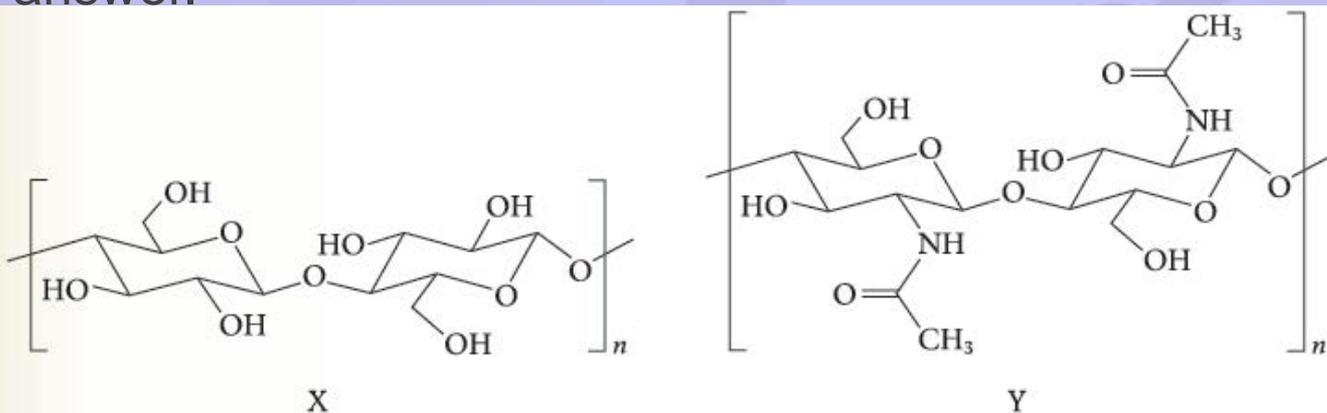




54.9 Applications of infrared spectroscopy (p.138)

Q (Example 54.1) (continued)

With reference to the information given in the table below, suggest which of the following structures (X and Y) may be the structure of chitin. Explain your answer.



Characteristic infrared absorption wavenumber ranges (stretching modes)

Bond	Compound type	Wavenumber range (cm ⁻¹)
C=C	alkenes	1 610–1 680
C=O	aldehydes, ketones, carboxylic acids and derivatives	1 680–1 800
C≡C	alkynes	2 070–2 250
C≡N	nitriles	2 200–2 280
O–H	acids (hydrogen-bonded)	2 500–3 300
O–H	alcohols, phenols (hydrogen-bonded)	3 230–3 670





54.9 Applications of infrared spectroscopy (p.138)

Q (Example 54.1) (continued)

A

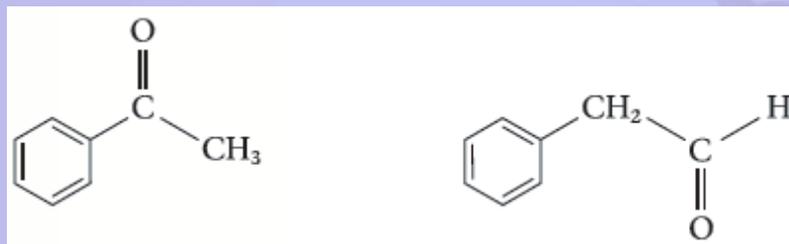
Y is the structure of chitin. The presence of an absorption peak within the range $1\ 680 - 1\ 800\ \text{cm}^{-1}$ shows the presence of C=O groups, ruling out the possibility of structure X.



54.9 Applications of infrared spectroscopy (p.138)

Q (Example 54.2)

The two compounds shown below are isomers.



With reference to the information given in the table below, suggest whether infrared spectroscopy can be used to distinguish the two compounds.

Characteristic infrared absorption wavenumber ranges (stretching modes)

Bond	Compound type	Wavenumber range (cm ⁻¹)
C=C	alkenes	1 610–1 680
C=O	aldehydes, ketones, carboxylic acids and derivatives	1 680–1 800
C≡C	alkynes	2 070–2 250
C≡N	nitriles	2 200–2 280
O–H	acids (hydrogen-bonded)	2 500–3 300
C–H	alkanes, alkenes, arenes	2 840–3 095
O–H	alcohols, phenols (hydrogen-bonded)	3 230–3 670
N–H	amines	3 350–3 500





54.9 Applications of infrared spectroscopy (p.138)

Q (Example 54.2) (continued)

A

The infrared spectra of both compounds have a strong absorption peak within the range $1\ 680 - 1\ 800\ \text{cm}^{-1}$ which is a characteristic of the C=O bond / carbonyl group.

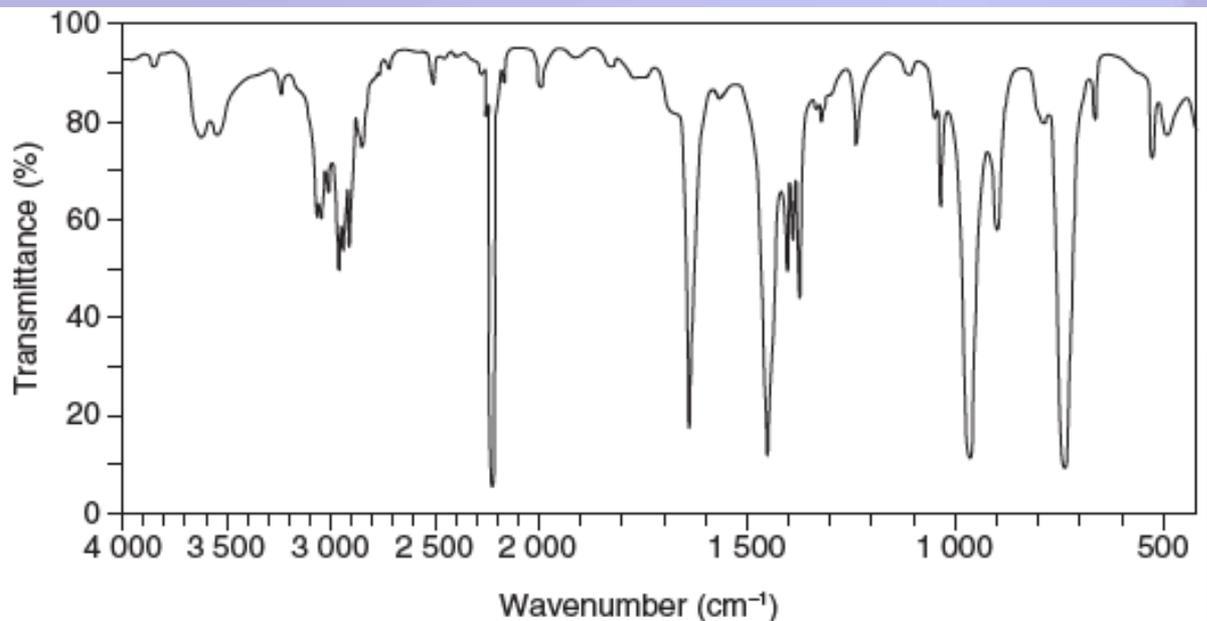
The two compounds do not have other different functional groups, and thus they cannot be distinguished by using the given information.



54.9 Applications of infrared spectroscopy (p.138)

Practice 54.2

1 Consider the infrared spectrum of but-2-enenitrile ($\text{CH}_3\text{CH}=\text{CHC}\equiv\text{N}$).



Strong absorption peak at about $2\,200\text{ cm}^{-1}$ is a characteristic of the $\text{C}\equiv\text{N}$ bond.

Strong absorption peak at about $1\,610\text{--}1\,680\text{ cm}^{-1}$ is a characteristic of the $\text{C}=\text{C}$ bond.

Identify TWO features of the infrared spectrum that support the fact that this is the infrared spectrum of but-2-enenitrile.
(Refer to the information given in Table 54.1.)



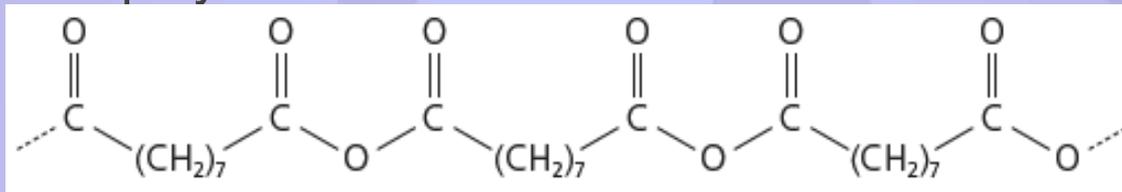
54.9 Applications of infrared spectroscopy

(p.138)

Practice 54.2 (continued)

2 The polyanhydride, PAPA, is used to form a protective coating around some anti-cancer drugs.

A section of the polymer chain of PAPA is shown below.



The PAPA coating is degradable and breaks down to form the dicarboxylic acid $\text{HOOC}(\text{CH}_2)_7\text{COOH}$.

a) Name the type of reaction that occurs when PAPA degrades. **Hydrolysis**

b) PAPA-coated tablets can be stored for a long time in blister packets.

Scientists can detect whether PAPA has degraded using infrared spectroscopy.

Outline how infrared spectroscopy could be used to determine if PAPA has degraded.

(Refer to the information given in Table 54.1.)

b) Observe whether there is a broad absorption peak within the range $2\,500\text{--}3\,300\text{ cm}^{-1}$ which corresponds to a O–H bond (acid) because degradation of PAPA gives a dicarboxylic acid.



54.10 Mass spectrometry (p.143)

- ◆ Mass spectrometry is a very powerful analytical tool that can provide information on relative atomic masses of elements, and relative molecular masses and structures of carbon compounds.
- ◆ The instrument used in mass spectrometry is called a **mass spectrometer** (質譜儀).



A mass spectrometer

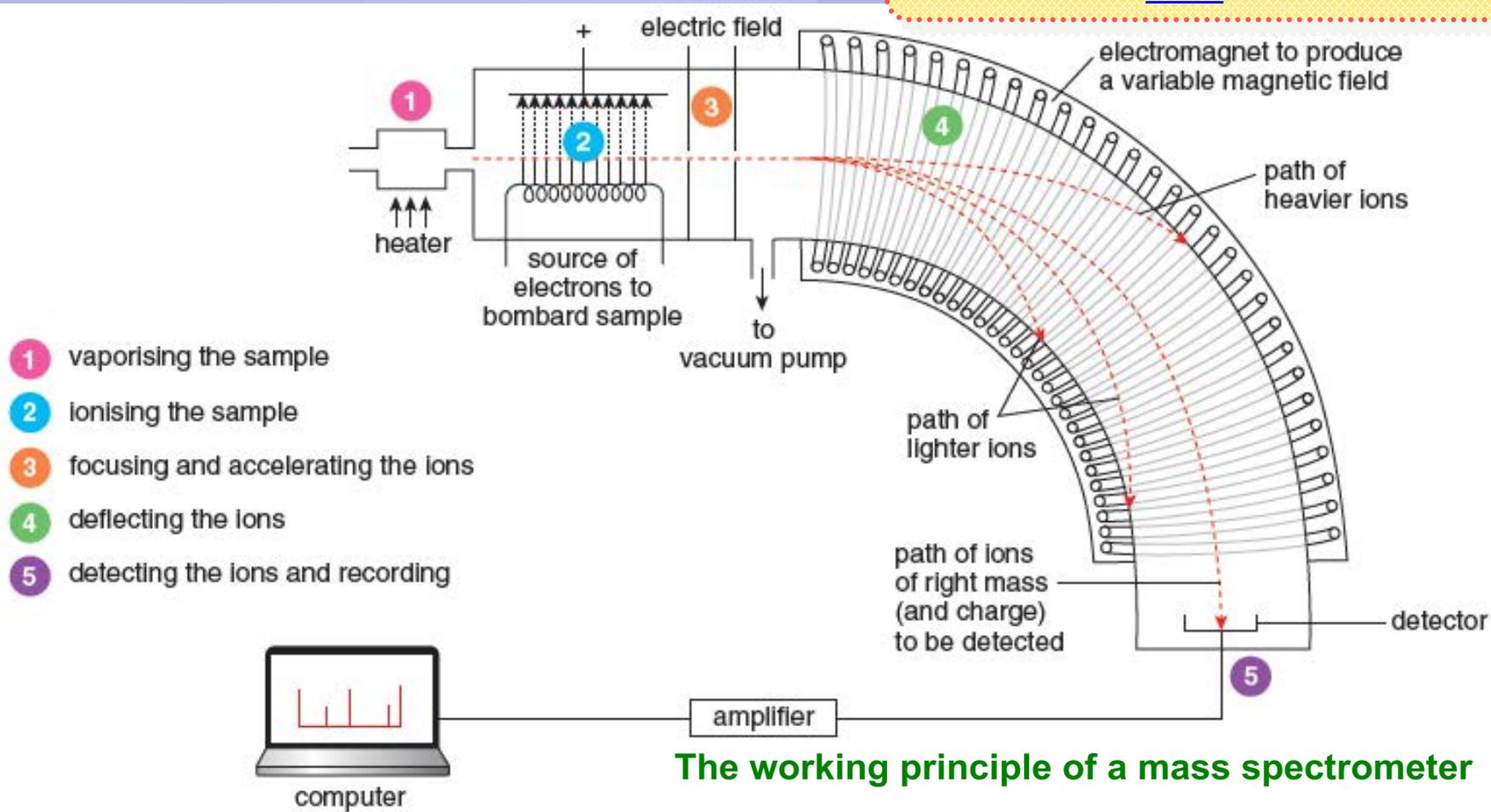


54.10 Mass spectrometry (p.143)

How a mass spectrometer works



How a mass spectrometer works [Ref.](#)



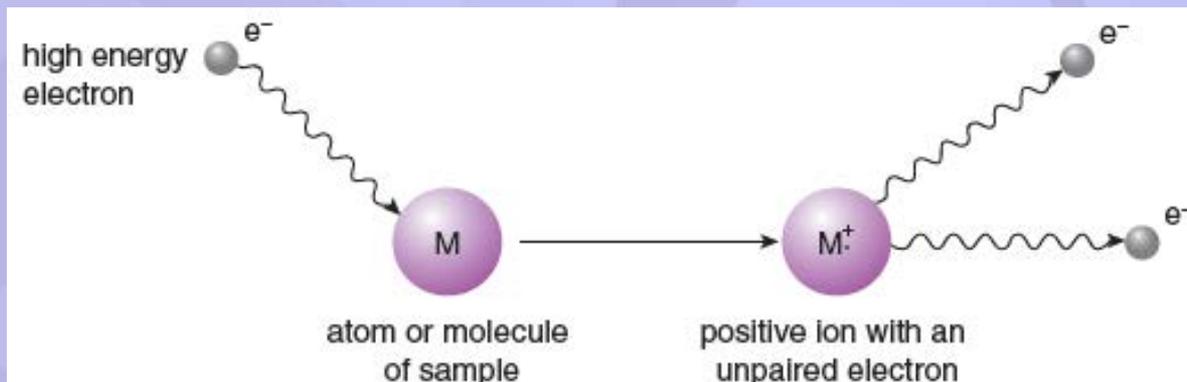


54.10 Mass spectrometry (p.143)

1 Vaporising the sample

A sample being analysed is injected into the chamber and heated until it changes to gaseous form. The sample being analysed can be an element or a compound.

2 Ionising the sample High energy electrons are fired at the gaseous sample. These knock off electrons from the sample, producing positive ions with unpaired electrons.



Atom or molecule of sample produces a positive ion after bombarded by a high energy electron



54.10 Mass spectrometry (p.143)

3 Focusing and accelerating the ions

Electrically charged plates are used to focus the positive ions into a beam and direct them down the instrument.

4 Deflecting the ions

The fast-moving ions are deflected by an electromagnet. The extents of deflection depend on the mass-to-charge ratio of the ions. If all ions have a +1 charge (which is usually the case), the extents of deflection only depend on their masses. The lighter ions are deflected more than the heavier.



54.10 Mass spectrometry (p.143)

5 Detecting the ions and recording

The deflected ions pass through a narrow slit and are collected on a detector connected to an amplifier. For a given strength of magnetic field, only ions of a certain mass pass through the slit and hit the detector. As the ions hit the detector, they cause a current to flow through the amplifier. The more ions there are, the larger the current.

- ◆ By varying the strength of the magnetic field, ions of different mass-to-charge ratios are allowed to pass successively through the slit. A mass spectrum, which shows the strength of the signal produced by ions of varying mass-to-charge ratio, is produced.



54.11 General information about a mass spectrum (p.145)

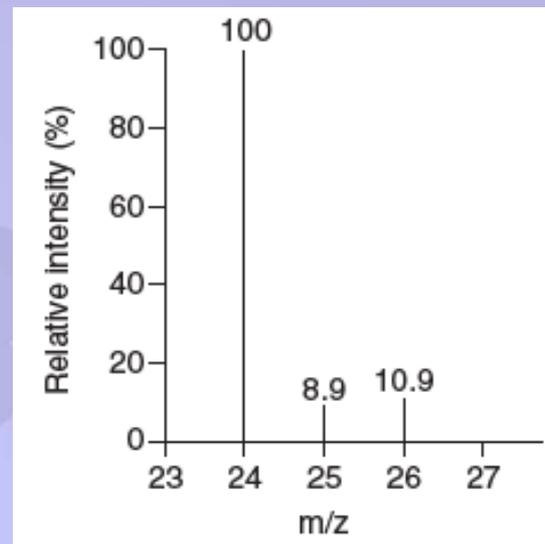
- ◆ A mass spectrum has a series of peaks where the vertical axis is relative intensity (%) and the horizontal axis is the mass-to-charge ratio (m/z).
- ◆ The most abundant ion gives the strongest signal which is set to 100% in the spectrum. The intensities of all other peaks are expressed as a percentage of this value.
- ◆ Since the charge on the ions is normally +1, the horizontal axis represents the relative mass of the species.



54.11 General information about a mass spectrum (p.145)

Mass spectrum of an element

- ◆ The figure shows the mass spectrum of naturally occurring magnesium. The numbers above the peaks indicate the relative abundance of each ion detected.



Mass spectrum of magnesium

- Magnesium has three isotopes as there are three peaks on the spectrum which correspond to each of the isotopes.
- The relative isotopic masses of these isotopes are 24, 25 and 26 as these are the m/z values for the isotopes.
- The most abundant magnesium has a relative isotopic mass of 24. This is the m/z value for the peak with the highest relative intensity.

Relative atomic mass of magnesium

$$= \frac{(24 \times 100) + (25 \times 8.9) + (26 \times 10.9)}{100 + 8.9 + 10.9}$$

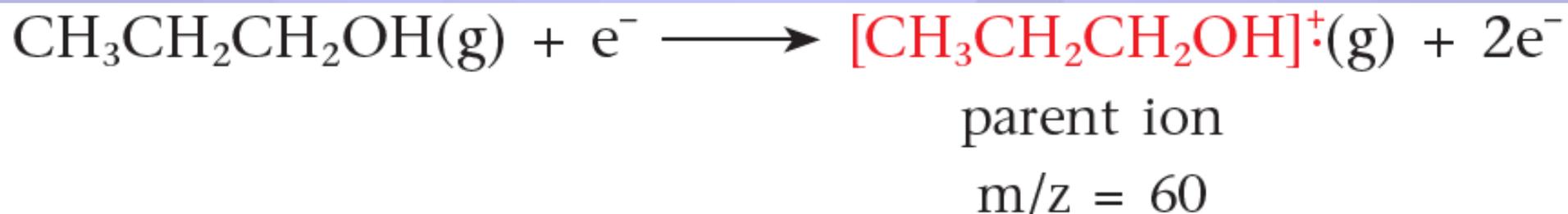
$$= 24.3$$



54.11 General information about a mass spectrum (p.145)

Mass spectrum of a carbon compound

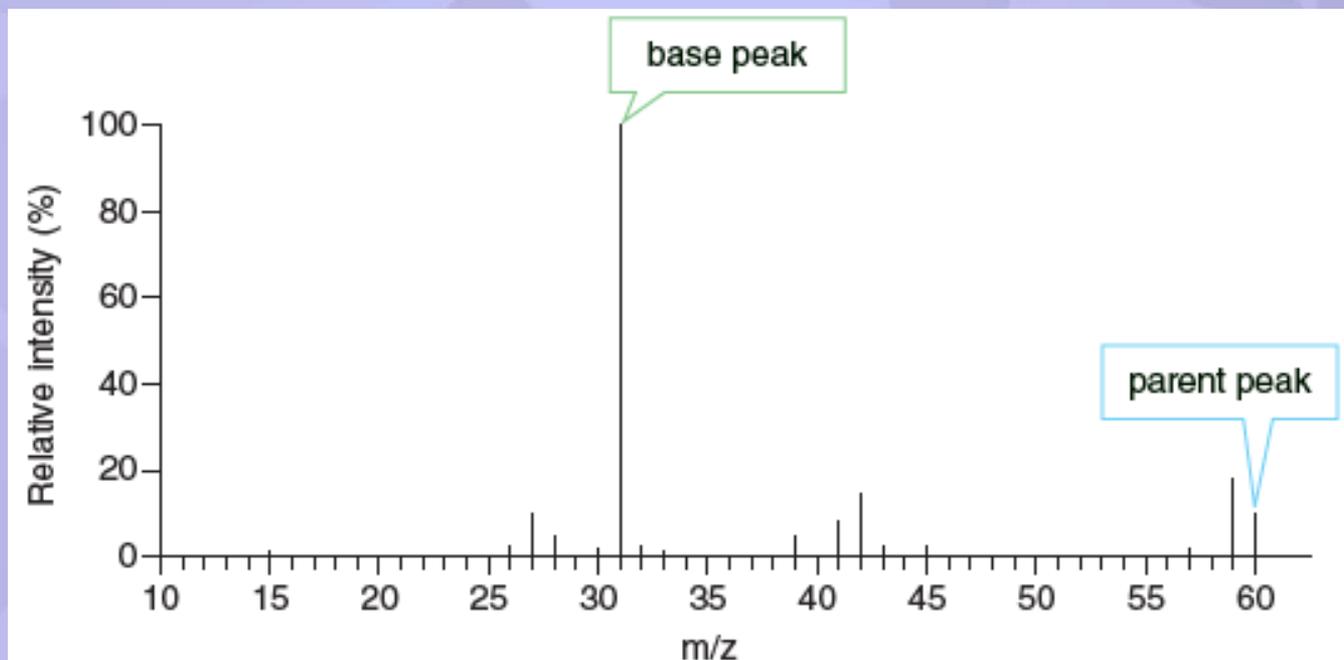
- ◆ The peak furthest to the right is the one with the greatest m/z value. This peak is the parent peak — the result of the molecule losing an electron in the mass spectrometer, forming a parent ion. The equation for this process, using propan-1-ol as an example, is:





54.11 General information about a mass spectrum (p.145)

- ◆ The parent peak is at an m/z value of 60. This shows that the relative molecular mass of propan-1-ol is 60.



Mass spectrum of propan-1-ol



54.11 General information about a mass spectrum (p.145)

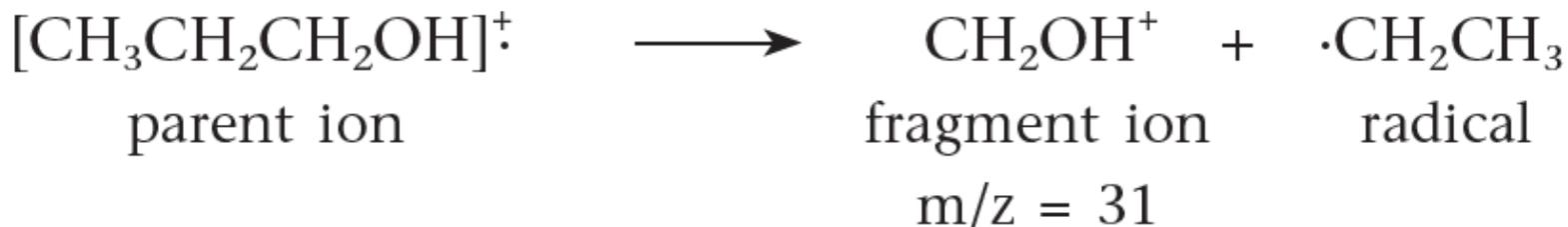
Fragmentation

- ◆ The peak with the greatest intensity is called the **base peak** (基本峰) which is usually not the parent peak. This peak corresponds to the most stable chemical species.
- ◆ In the mass spectrometer, some parent ions break down into smaller pieces known as fragments in a process called **fragmentation** (碎裂).
- ◆ The other peaks in a mass spectrum are caused by **fragment ions** (碎塊離子), formed from the breakdown of the parent ion.



54.11 General information about a mass spectrum (p.145)

- ◆ The simplest fragmentation breaks a parent ion into two chemical species — a positively charged fragment ion and a radical.
- ◆ Any positive ions formed will be detected by the mass spectrometer, but the uncharged radicals are not detected.
- ◆ In the mass spectrum for propan-1-ol, the base peak has an m/z value of 31. The equation below shows the possible structure of this fragment ion and its formation from the parent ion.



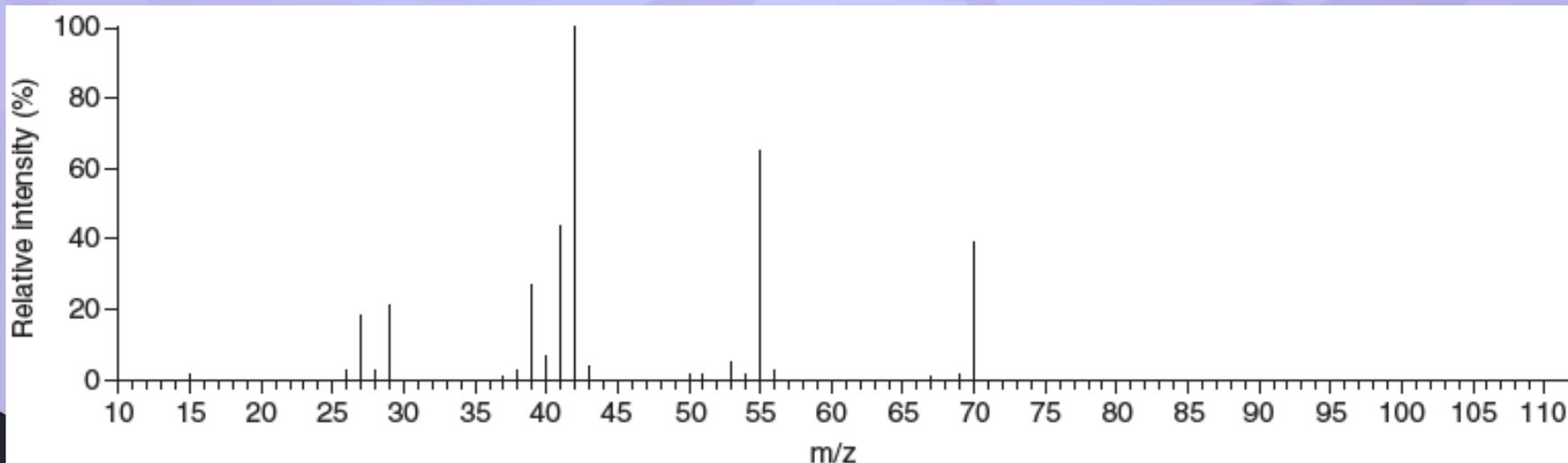


54.11 General information about a mass spectrum (p.145)

Practice 54.3

Use the mass spectra below to identify the parent peaks and hence deduce the relative molecular masses of compounds A and B.

Compound A



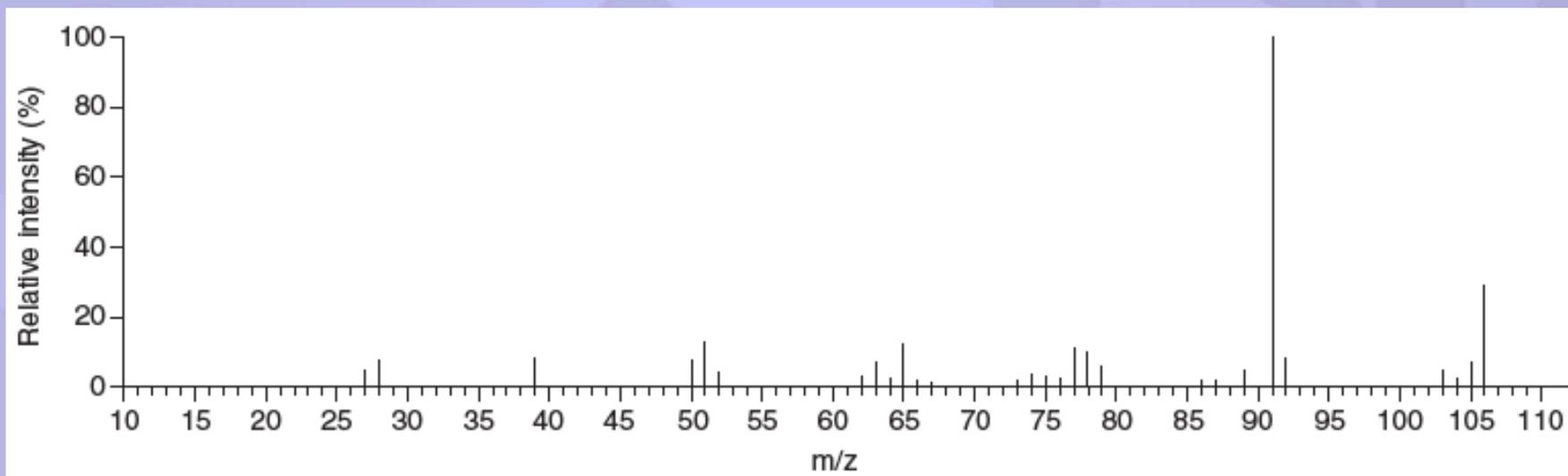
Relative molecular mass of compound A = 70



54.11 General information about a mass spectrum (p.145)

Practice 54.3 (continued)

Compound B



Relative molecular mass of compound B = 106



54.12 Using fragmentation patterns to identify carbon compounds (p.148)

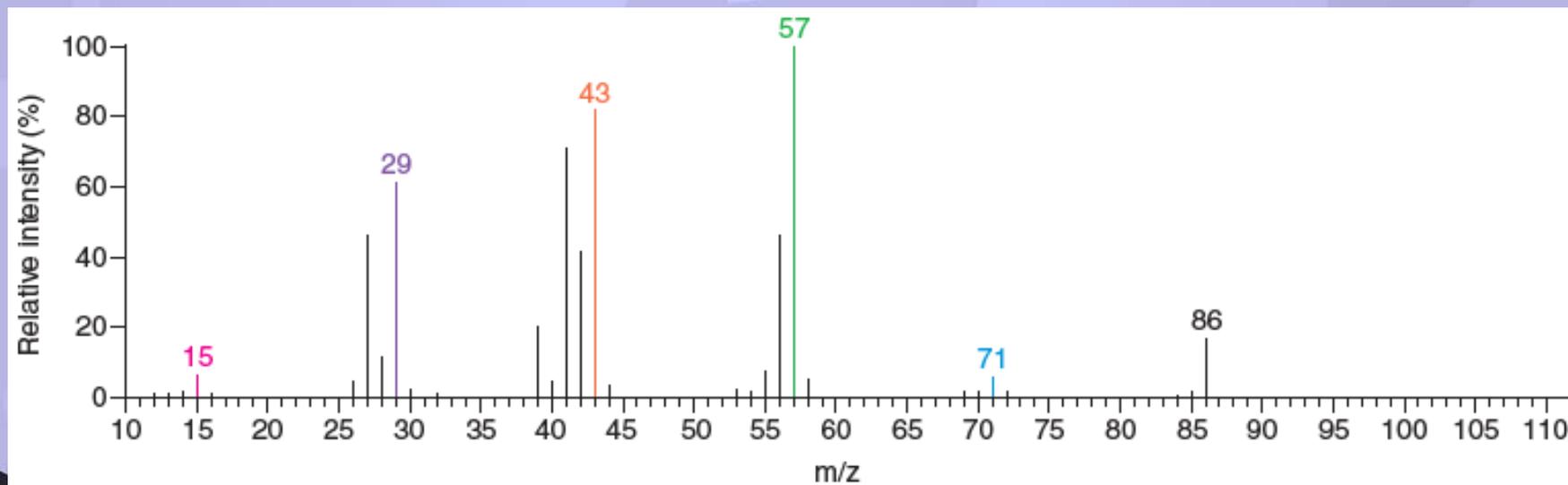
- ◆ The mass spectrum of each compound is unique, as molecules will all fragment in slightly different ways depending on their structures.
- ◆ Two compounds may have the same molecular mass and the same parent peak, the fragment ions found in their spectra may be different.



54.12 Using fragmentation patterns to identify carbon compounds (p.148)

Fragmentation patterns of hexane and 2-methylpentane

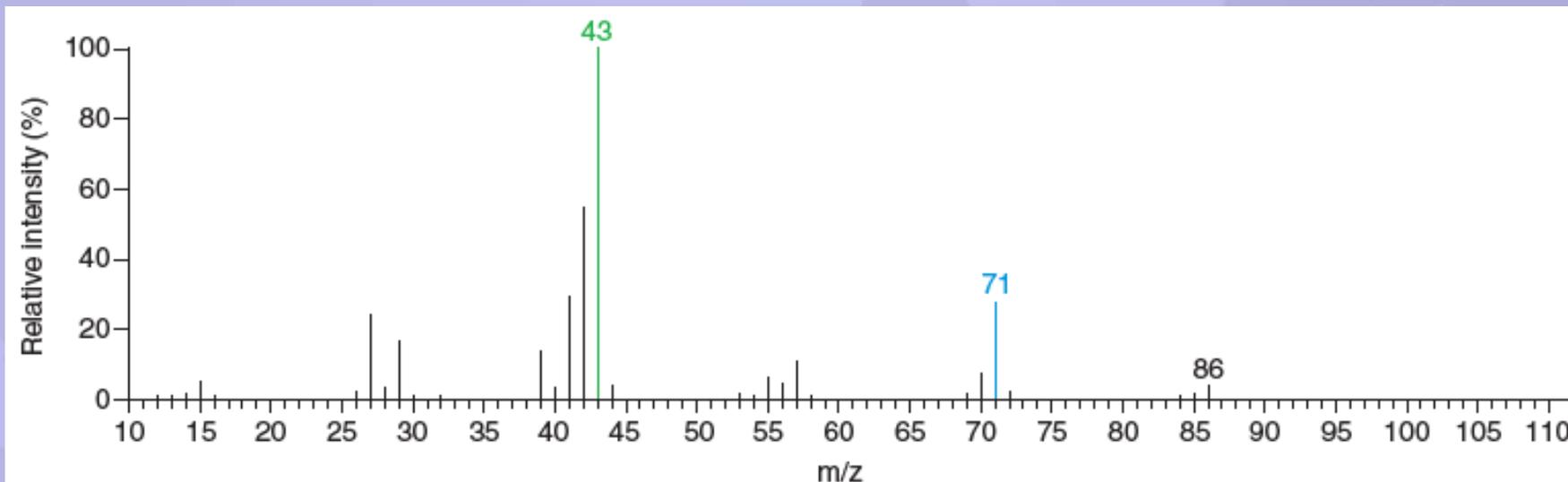
- The mass spectra of hexane and 2-methylpentane have the parent peak at $m/z = 86$ but the **fragmentation patterns (碎裂模式)** are different.



Mass spectrum of hexane



54.12 Using fragmentation patterns to identify carbon compounds (p.148)

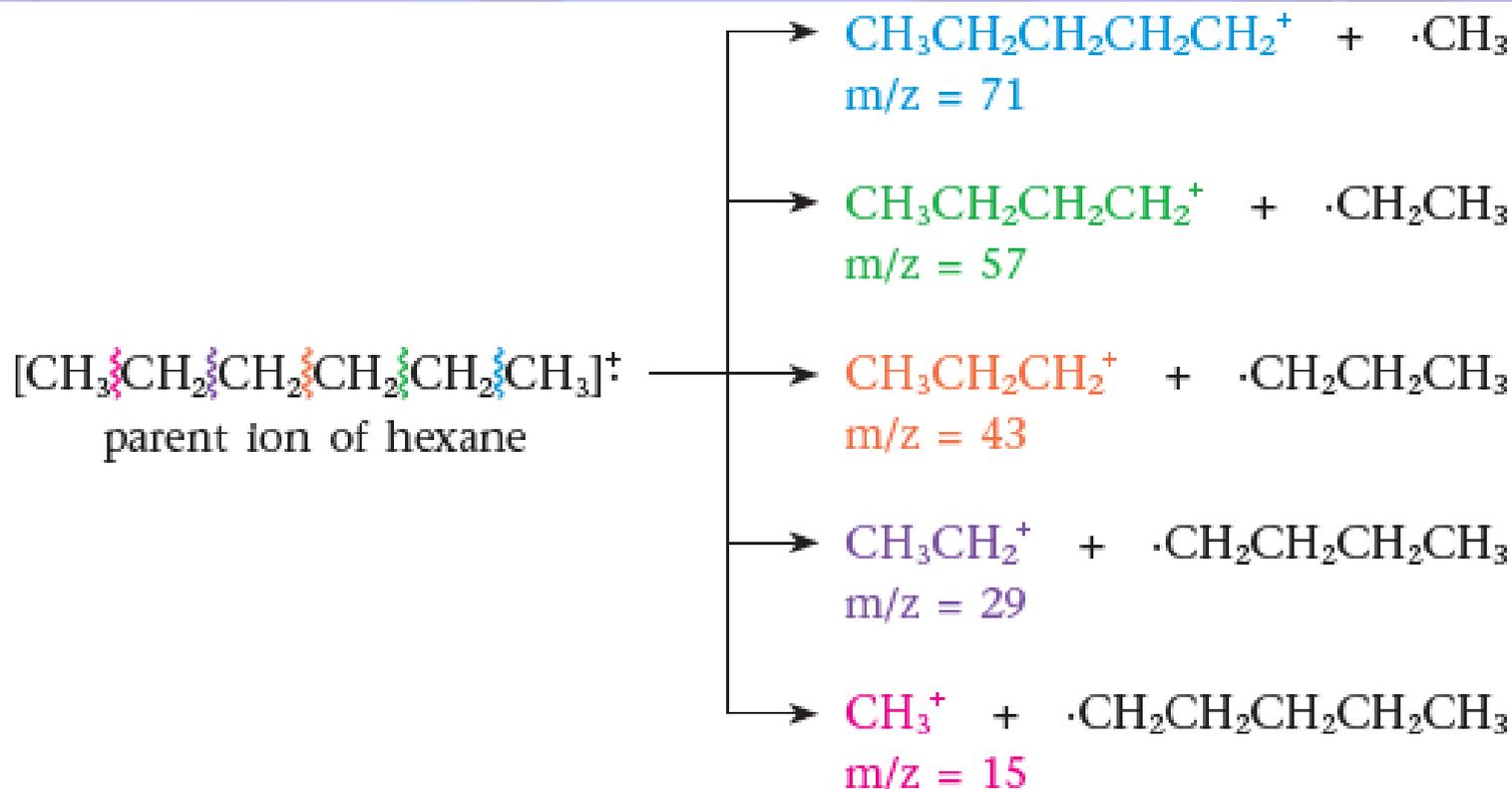


Mass spectrum of 2-methylpentane



54.12 Using fragmentation patterns to identify carbon compounds (p.148)

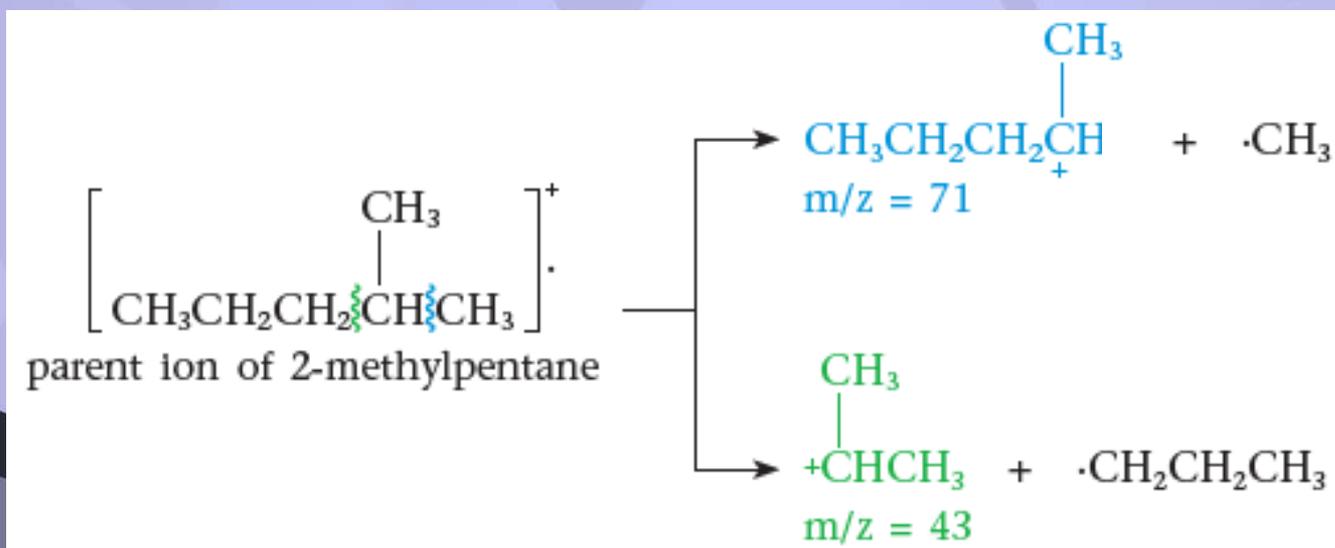
- The parent ion of hexane might fragment by breaking any of its carbon-carbon bonds:





54.12 Using fragmentation patterns to identify carbon compounds (p.148)

- ◆ Chain branching in alkanes increases the likelihood of splitting at a branch point because a more stable carbocation results.
- ◆ The peak at $m/z = 71$ is stronger than that in the mass spectrum of hexane and the base peak is at $m/z = 43$. These peaks correspond to the secondary carbocations produced by the following fragmentations:

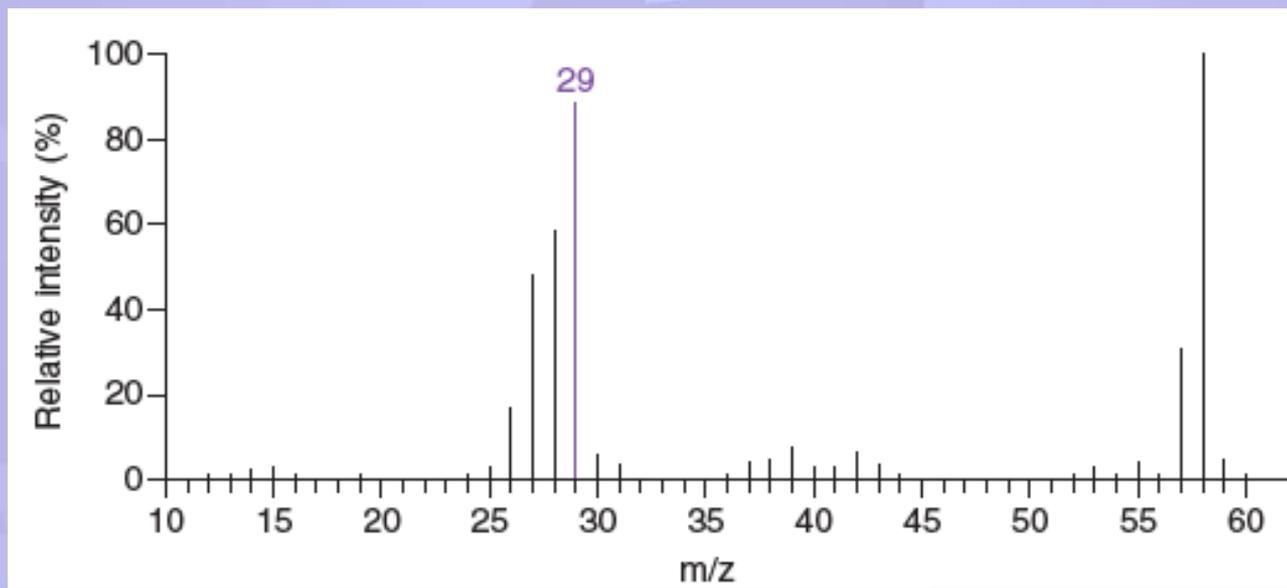




54.12 Using fragmentation patterns to identify carbon compounds (p.148)

Fragmentation patterns of propanal and propanone

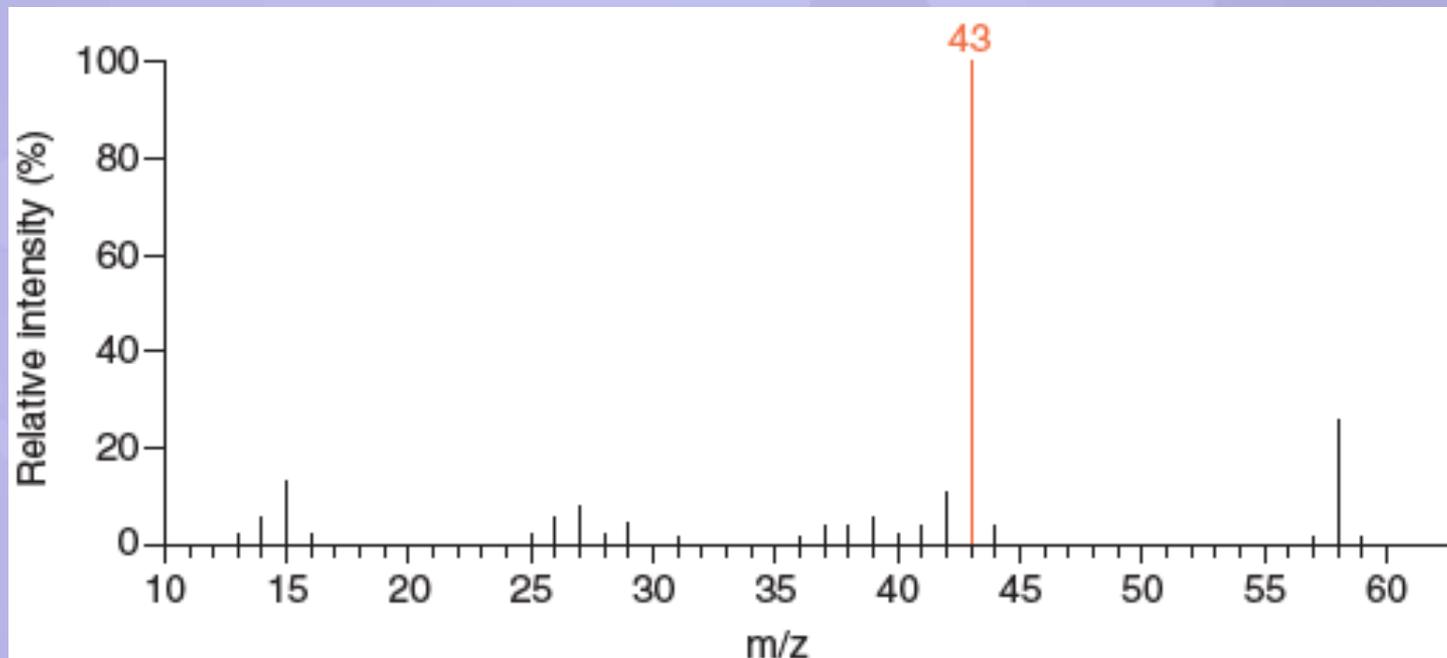
- The mass spectra of propanal and propanone — two isomers of C_3H_6O have the parent peak at $m/z = 58$ but the fragmentation patterns are different.



Mass spectrum of propanal



54.12 Using fragmentation patterns to identify carbon compounds (p.148)

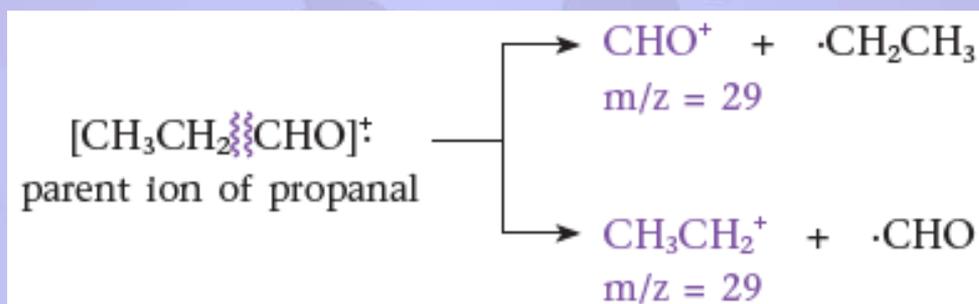


Mass spectrum of propanone



54.12 Using fragmentation patterns to identify carbon compounds (p.148)

- One obvious difference is a strong peak at $m/z = 29$ in the spectrum of propanal, which is not present in the spectrum of propanone. This could be caused by either CHO^+ ion or CH_3CH_2^+ ion or by both of them.

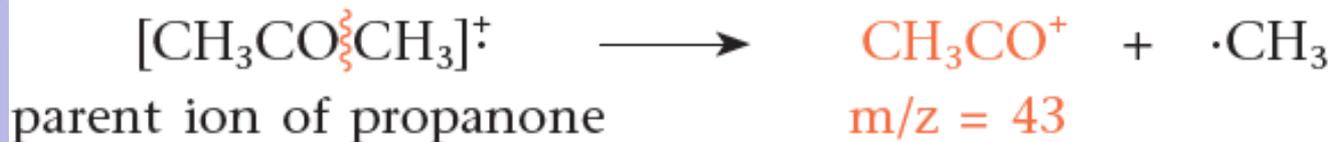


- The other obvious difference is a strong peak at $m/z = 43$ in the mass spectrum of propanone, which is not present in the mass spectrum of propanal.



54.12 Using fragmentation patterns to identify carbon compounds (p.148)

- ◆ Fragmentation of the parent ion of a ketone often occurs at the carbon-carbon bond next to the carbonyl group, generating RCO^+ ion.
- ◆ The peak at $m/z = 43$ corresponds to the CH_3CO^+ ion, which is produced by this fragmentation:

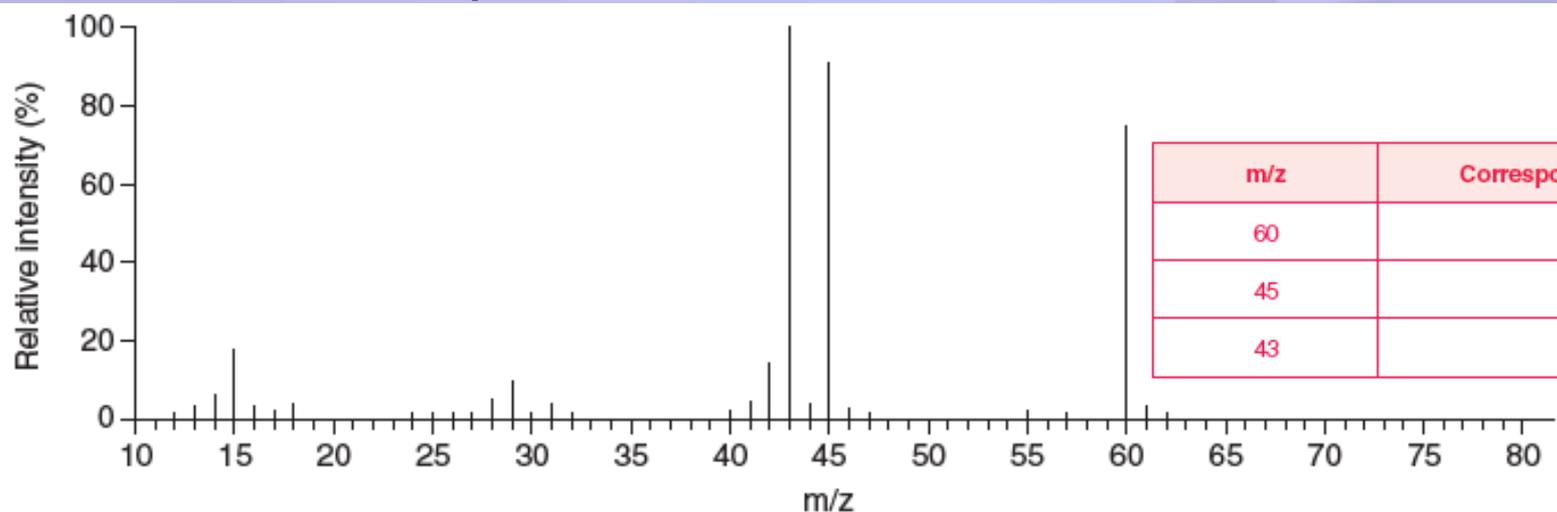




54.12 Using fragmentation patterns to identify carbon compounds (p.148)

Practice 54.4

1 The mass spectrum of ethanoic acid is shown below.



m/z	Corresponding chemical species
60	$[\text{CH}_3\text{COOH}]^+$
45	COOH^+
43	CH_3CO^+

The mass spectrum of ethanoic acid shows a parent peak at $m/z = 60$, and strong peaks at each of $m/z = 43$ and 45 .

Suggest ONE chemical species corresponding to each of the signals.

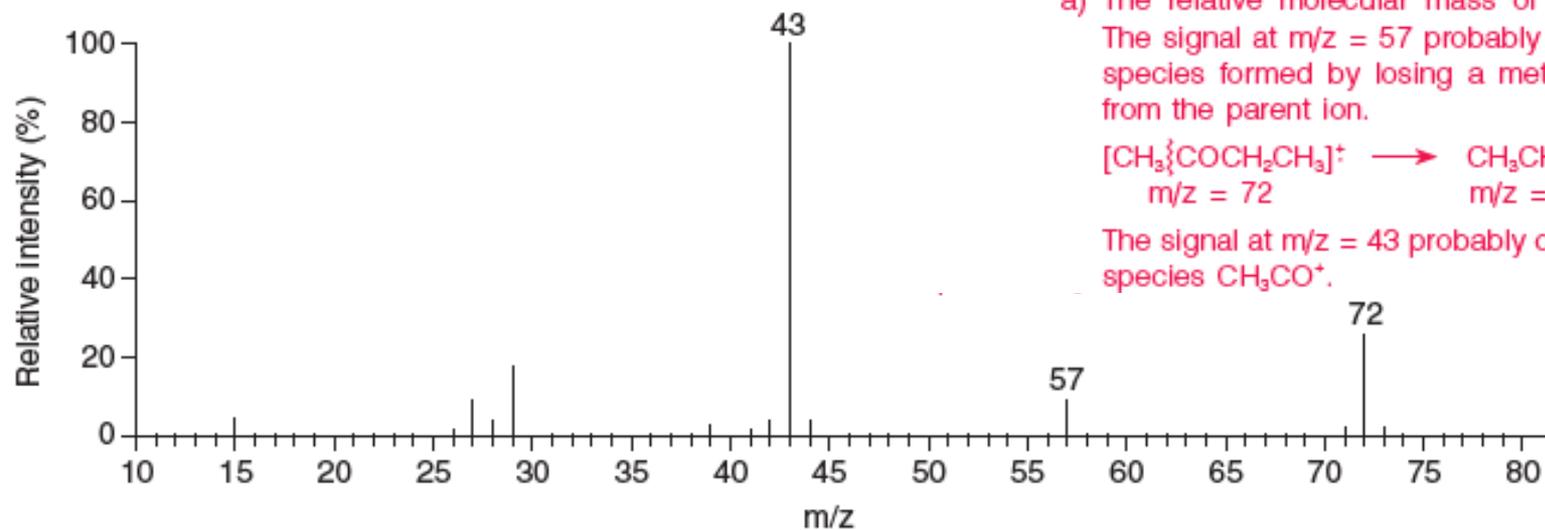
(Relative atomic masses: $\text{H} = 1.0$, $\text{C} = 12.0$, $\text{O} = 16.0$)



54.12 Using fragmentation patterns to identify carbon compounds (p.148)

Practice 54.4 (continued)

2 The mass spectrum of a compound is shown below. The compound is known to be either butanal or butanone.



a) The relative molecular mass of butanone / butanal is 72. The signal at $m/z = 57$ probably corresponds to a chemical species formed by losing a methyl radical ($72 - 57 = 15$) from the parent ion.



The signal at $m/z = 43$ probably corresponds to the chemical species CH_3CO^+ .

a) Suggest ONE chemical species corresponding to each of the signals at $m/z = 43$ and 57.

b) Suggest whether the compound is butanal or butanone.

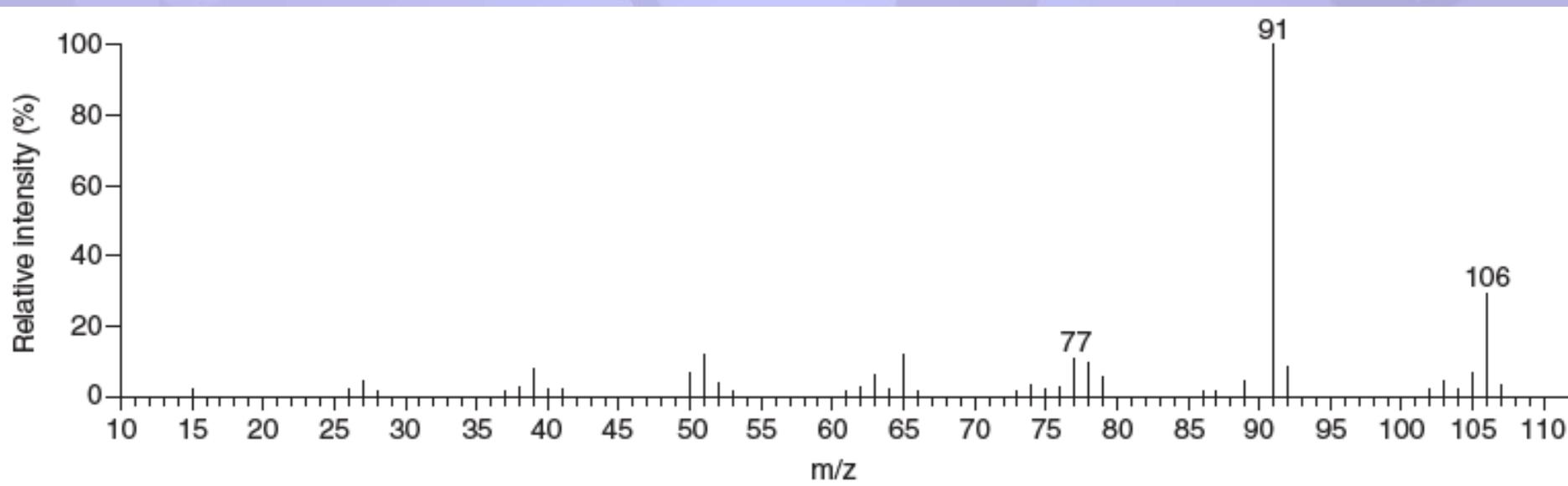
(Relative atomic masses: H 1.0, C = 12.0, O = 16.0) **The compound is butanone.**



54.12 Using fragmentation patterns to identify carbon compounds (p.148)

Fragmentation patterns of aromatic compounds

- The mass spectrum of ethylbenzene ($C_6H_5CH_2CH_3$). The parent peak is at $m/z = 106$.

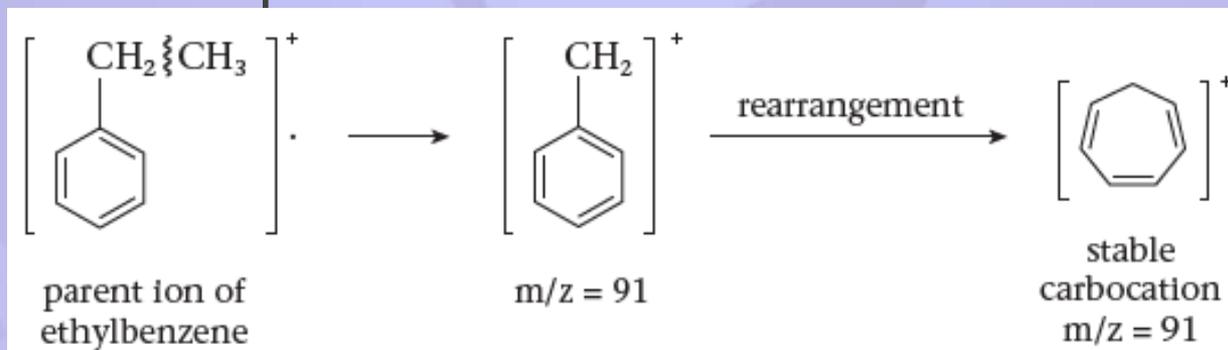


Mass spectrum of ethylbenzene



54.12 Using fragmentation patterns to identify carbon compounds (p.148)

- The parent ion of ethylbenzene undergoes the fragmentation shown below to yield the $C_6H_5CH_2^+$ ion which rearranges to give a relatively stable carbocation $C_7H_7^+$. This ion gives rise to the characteristic peak at $m/z = 91$.



- The peak at $m/z = 77$ corresponds to the $C_6H_5^+$ ion, which is produced by the loss of a $\cdot CH_2CH_3$ radical from the parent ion.
- Peaks at m/z values of 77 and 91 are frequently present in the mass spectra of aromatic compounds.



54.12 Using fragmentation patterns to identify carbon compounds (p.148)

Typical fragment ions produced in a mass spectrometer

- ◆ Typical fragment ions produced in a mass spectrometer and their corresponding m/z values are listed below.

Ion	Mass-to-charge ratio (m/z)
CH_3^+	15
C_2H_5^+	29
CH_3CO^+	43
C_3H_7^+	43
C_4H_9^+	57
$\text{CH}_3\text{CH}_2\text{CO}^+$	57
C_6H_5^+	77
$\text{C}_6\text{H}_5\text{CH}_2^+$	91



54.12 Using fragmentation patterns to identify carbon compounds (p.148)

Q (Example 54.3) (continued)

A

Any two of the following:

- In the mass spectrum of X, a peak appears at $m/z = 43$ for CH_3CO^+ ion, which is not present in the mass spectrum of Y.
- In the mass spectrum of Y, a peak appears at $m/z = 119$ for $\text{C}_6\text{H}_5\text{CH}_2\text{CO}^+$ ion, which is not present in the mass spectrum of X.
- In the mass spectrum of X, a peak appears at $m/z = 93$ for $\text{C}_6\text{H}_5\text{O}^+$ ion, which is not present in the mass spectrum of Y.
- In the mass spectrum of Y, a peak appears at $m/z = 91$ for $\text{C}_6\text{H}_5\text{CH}_2^+$ ion, which is not present in the mass spectrum of X.
- In the mass spectrum of Y, a peak appears at $m/z = 45$ for COOH^+ ion, which is not present in the mass spectrum of X.



54.12 Using fragmentation patterns to identify carbon compounds (p.148)

- ◆ A hazard is something with the potential to cause harm, including injury to persons, or damage to property or equipment. A risk is the likelihood of a hazard causing harm in practice.
- ◆ To carry out a risk assessment to identify the hazards and take appropriate precautions to reduce the risk before conducting an experiment. Below are some examples.
 - Almost all organic chemicals are flammable. Thus, do not heat flasks and test tubes containing them directly with a Bunsen flame. Use a hot water bath or an electric heater (reduces risk).
 - If a chemical can be absorbed through the skin, wear protective gloves.
 - If a chemical has a harmful, irritating or toxic vapour, carry out the experiment inside a fume cupboard.
 - If a chemical is corrosive, harmful, irritating or toxic, wear protective gloves and take extra care.
 - Any substance suspected of being a carcinogen must not be used in a school laboratory.



54.12 Using fragmentation patterns to identify carbon compounds (p.148)

Q (Example 54.4)

Compound X contains a $-\text{C}_6\text{H}_5$ group. Two chemical tests are performed on X and the results are as follows:

Test 1: X turns acidified aqueous solution of potassium dichromate green.

Test 2: X gives a positive result when tested with Tollens' reagent.

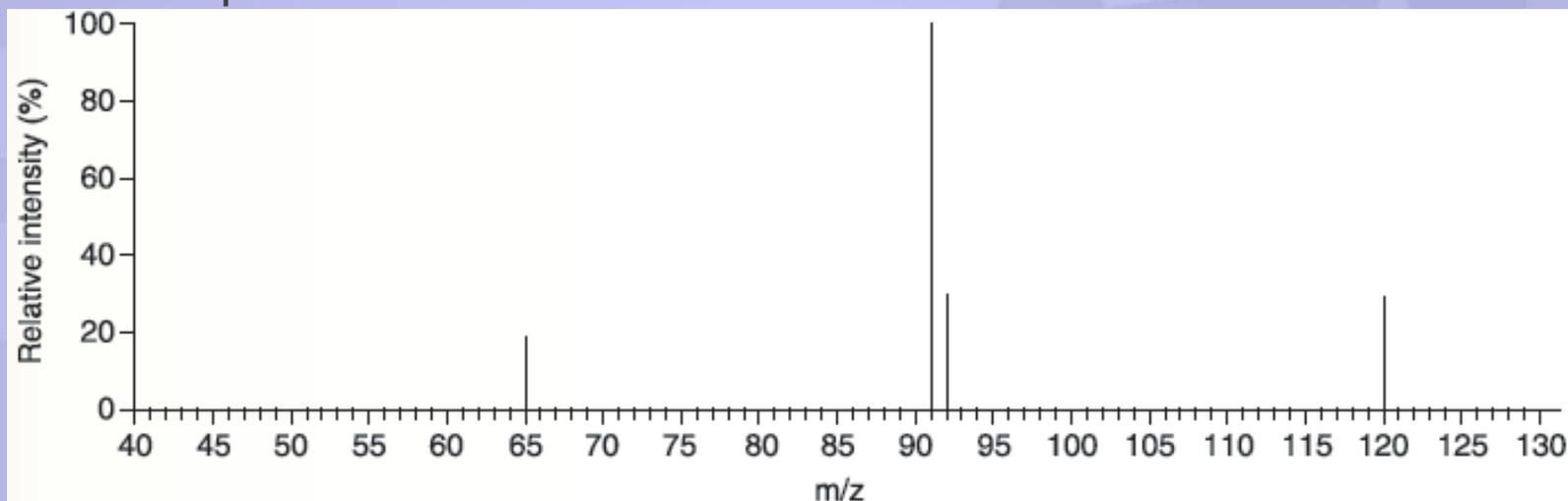
- a) With reference to the result of *Test 1* only, suggest TWO functional groups that X may have.
- b)
 - i) What is the purpose of using Tollens' reagent in *Test 2*?
 - ii) State the expected observation for X.
- c) With reference to the results of both *Test 1* and *Test 2*, suggest ONE functional group that may be present in X.



54.12 Using fragmentation patterns to identify carbon compounds (p.148)

Q (Example 54.4) [\(continued\)](#)

d) The mass spectrum of X is shown below:



- Identify the parent peak and hence deduce the relative molecular mass of X.
 - Suggest one chemical species corresponding to the signal at $m/z = 91$.
- e) Draw a possible structure of X.



54.12 Using fragmentation patterns to identify carbon compounds (p.148)

Q (Example 54.4) (continued)

A

- a) Hydroxyl group
Aldehyde group
- b) i) To test for the presence of aldehyde group.
ii) A silver mirror forms on the wall of the reaction vessel.
- c) Aldehyde group
- d) i) The parent peak is at an m/z value of 120. Hence the relative molecular mass of X is 120.
ii) The signal at $m/z = 91$ suggests the presence of $C_6H_5CH_2^+$ ion.

e)

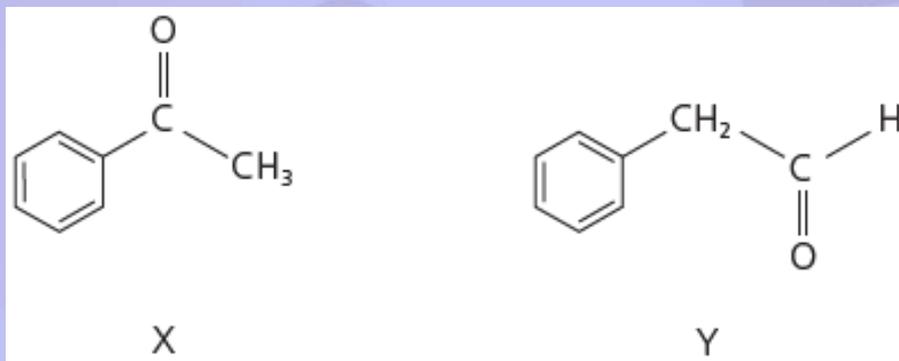




54.12 Using fragmentation patterns to identify carbon compounds (p.148)

Practice 54.5

1 Compounds X and Y are isomers.



Suggest, with explanation, how X and Y can be differentiated from their respective mass spectra.

(Relative atomic masses: H = 1.0, C = 12.0, O = 16.0)

A significant peak appears at $m/z = 105$ ($C_6H_5CO^+$) or $m/z = 43$ (CH_3CO^+) in the mass spectrum of X only.

A significant peak appears at $m/z = 91$ ($C_6H_5CH_2^+$) or $m/z = 29$ (CHO^+) in the mass spectrum of Y only.



54.12 Using fragmentation patterns to identify carbon compounds (p.148)

Practice 54.5 (continued)

2 Compound X has the empirical formula C_4H_4O .

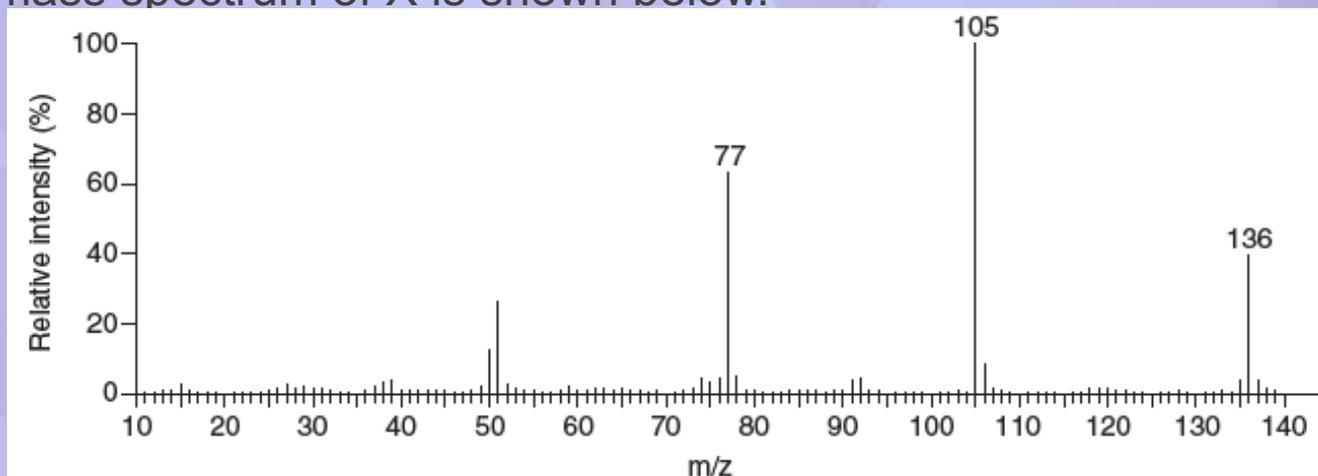
X is a fruity smell liquid.

X gives a negative result when tested with 2,4-dinitrophenylhydrazine.

X does not give effervescence when shaken with $Na_2CO_3(aq)$.

a) What functional group may be present in X?

b) The mass spectrum of X is shown below.



i) Identify the parent peak and hence deduce the molecular formula of X.

ii) Suggest ONE chemical species corresponding to each of the signals at $m/z = 77$ and 105.

c) Draw a possible structure of X.



54.12 Using fragmentation patterns to identify carbon compounds (p.148)

Practice 54.5 (continued)

2 a) X gives a negative result when tested with 2,4-dinitrophenylhydrazine.

It can be deduced that X is NOT a carbonyl compound.

X does not give effervescence when shaken with $\text{Na}_2\text{CO}_3(\text{aq})$. It can be deduced that X does NOT contain a $-\text{COOH}$ group.

X has a fruity smell. It is probably an ester.

An ester group may be present in X.

b) i) Relative molecular mass of X is 136.

Let $(\text{C}_4\text{H}_4\text{O})_n$ be the molecular formula of X.

Relative molecular mass of X = 136 = $n(4 \times 12.0 + 4 \times 1.0 + 16.0)$

$$136 = 68n$$

$$n = 2$$

\therefore the molecular formula of X is $\text{C}_8\text{H}_8\text{O}_2$.



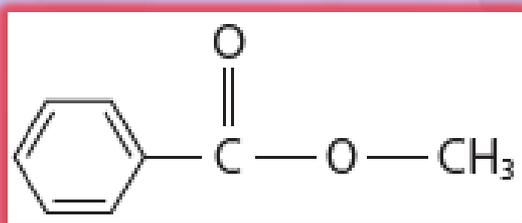
54.12 Using fragmentation patterns to identify carbon compounds (p.148)

Practice 54.5 (continued)

2 b) ii)

Signal	Corresponding chemical species
$m/z = 77$	$C_6H_5^+$
$m/z = 105$	$C_6H_5CO^+$

c)





54.13 Applications of mass spectrometry (p.157)

- testing athletes for the presence of illegal performance-enhancing drugs;
- monitoring and tracking pollutants in the air or in water supplies;
- detecting toxins in food;
- locating oil deposits by testing rock samples;
- determining the extent of damage to human genes due to the environment.

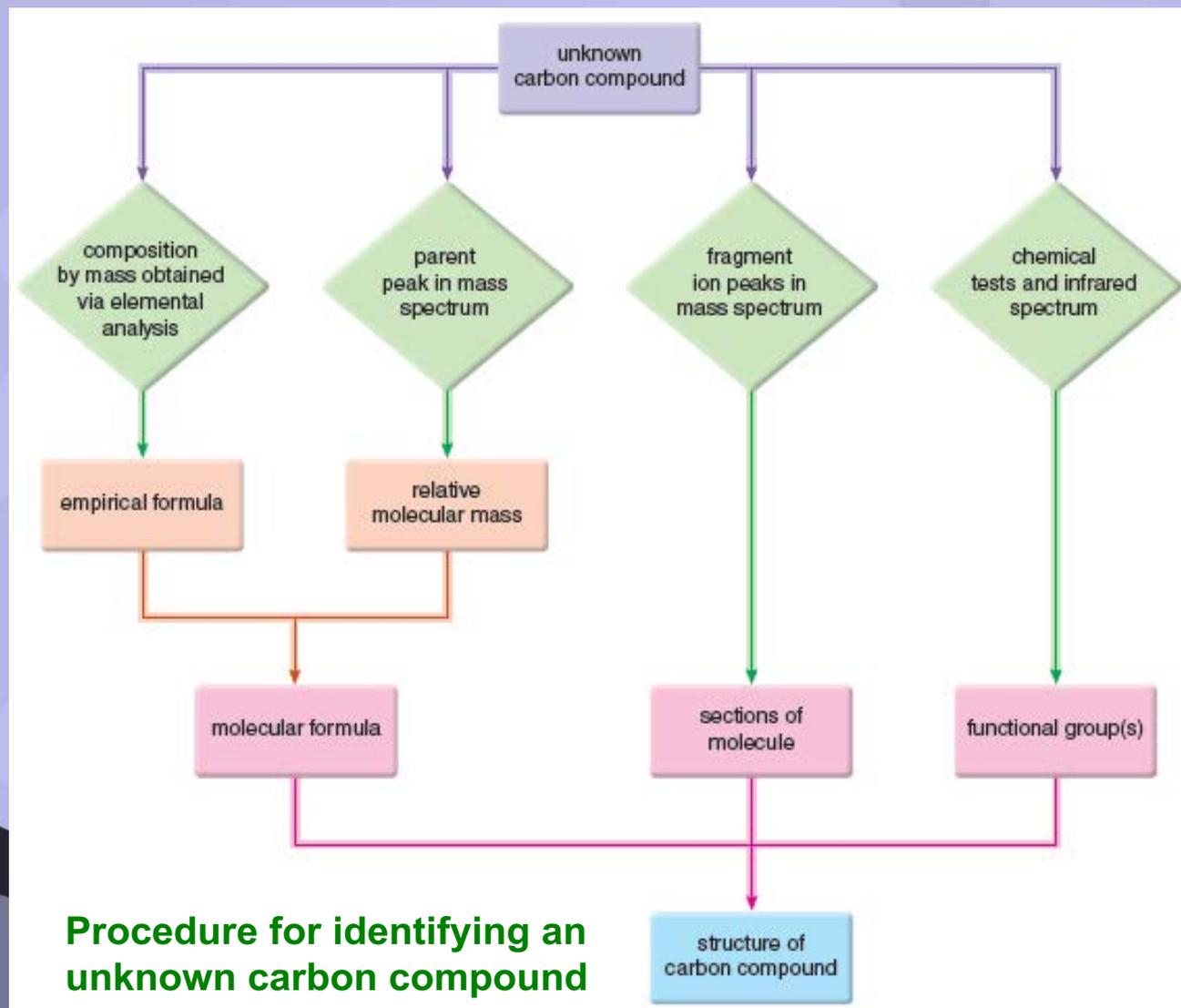


54.14 Identifying unknown carbon compounds by combined techniques (p.157)

- ◆ Analytical techniques are rarely used singly. Often, data from a number of different techniques are used to identify carbon compounds and determine their structures.
- ◆ A typical sequence for identification would include all of the following.
 - Elemental analysis — use of percentage composition data to determine the empirical formula.
 - Mass spectrometry — use of the parent peak from a mass spectrum to determine the relative molecular mass; use of fragment ions to identify sections of a molecule, and comparison of the mass spectra obtained to those in a database to identify unknown compounds.
 - Infrared spectroscopy — use of absorption peaks from an infrared spectrum to identify bonds and functional groups present in the molecule.
- ◆ Once you have both the empirical formula and the relative molecular mass of a compound, you can determine the molecular formula of your unknown compound. By then using evidence from the infrared spectrum, it may be possible to identify an unknown compound.



54.14 Identifying unknown carbon compounds by combined techniques (p.157)



Procedure for identifying an unknown carbon compound

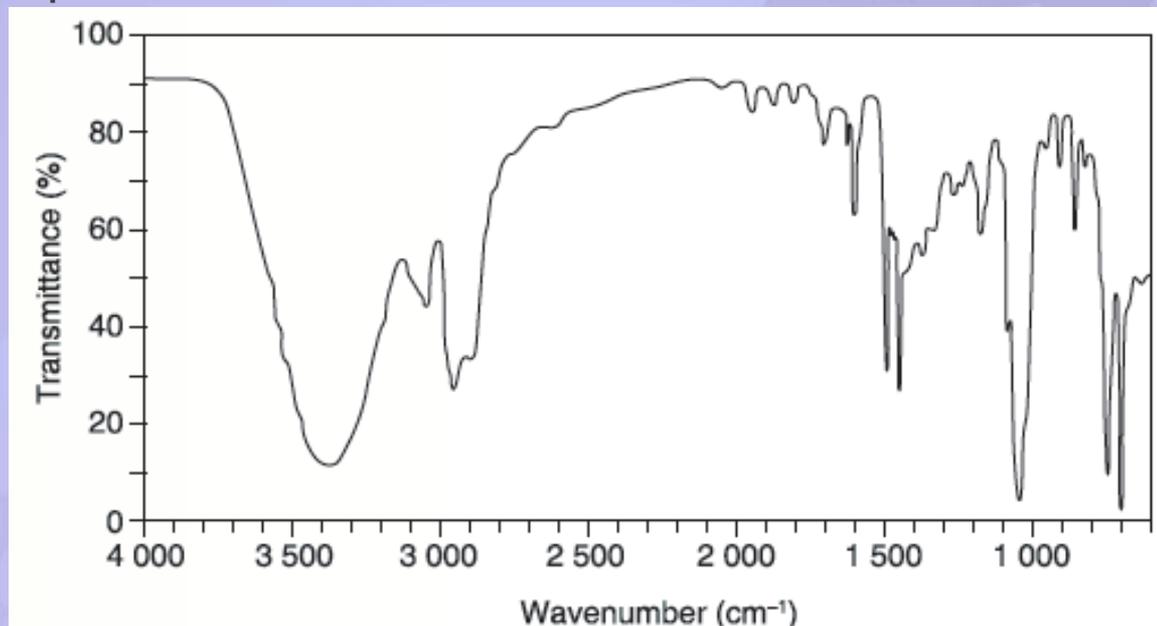


54.14 Identifying unknown carbon compounds by combined techniques (p.157)

Q (Example 54.5)

Under room temperature, compound T ($C_xH_yO_z$) is a colourless liquid.

a) The infrared spectrum of T is shown below.



Deduce the functional group(s) that T may have.

(Refer to the information given in Table 54.1.)



54.14 Identifying unknown carbon compounds by combined techniques (p.157)

Q (Example 54.5) (continued)

b) Elemental analysis of T gave the following percentage composition by mass:

carbon 77.8% hydrogen 7.4% oxygen 14.8%

Calculate the empirical formula of T.

c) The mass spectrum of T shows a parent peak at $m/z = 108$ and peaks at $m/z = 77$ and 91 .

i) Deduce the molecular formula of T.

ii) Suggest ONE chemical species corresponding to each of the signals at $m/z = 77$ and 91 .

d) Draw a possible structure of T.



54.14 Identifying unknown carbon compounds by combined techniques (p.157)

Q (Example 54.5) (continued)

A

- a) The spectrum has a broad and strong absorption peak at about $3\,230 - 3\,670\text{ cm}^{-1}$, which corresponds to O–H stretching. The spectrum does not show an absorption peak at about $1\,680 - 1\,800\text{ cm}^{-1}$, ruling out the presence of a C=O bond. Thus, the compound may contain a hydroxyl group.
- b) There are 77.8 g of carbon, 7.4 g of hydrogen and 14.8 g of oxygen in 100 g of T.

	Carbon	Hydrogen	Oxygen
Mass of element	77.8 g	7.4 g	14.8 g
Relative atomic mass	12.0	1.0	16.0
Number of moles of atoms	$\frac{77.8\text{ g}}{12.0\text{ g mol}^{-1}} = 6.48\text{ mol}$	$\frac{7.4\text{ g}}{1.0\text{ g mol}^{-1}} = 7.4\text{ mol}$	$\frac{14.8\text{ g}}{16.0\text{ g mol}^{-1}} = 0.925\text{ mol}$
Mole ratio of atoms	$\frac{6.48\text{ mol}}{0.925\text{ mol}} = 7$	$\frac{7.4\text{ mol}}{0.925\text{ mol}} = 8$	$\frac{0.925\text{ mol}}{0.925\text{ mol}} = 1$



54.14 Identifying unknown carbon compounds by combined techniques (p.157)

Q (Example 54.5) [\(continued\)](#)

A

c) i) Let $(C_7H_8O)_n$ be the molecular formula of T.

$$\begin{aligned}\text{Relative molecular mass of T} &= n(7 \times 12.0 + 8 \times 1.0 + 16.0) \\ &= 108n\end{aligned}$$

$$\text{i.e. } 108n = 108$$

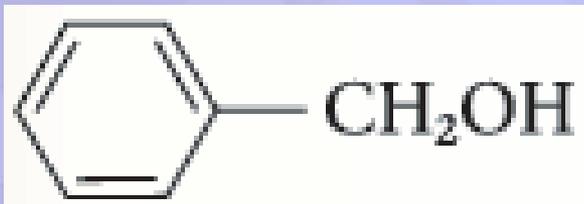
$$n = 1$$

\therefore the molecular formula of T is C_7H_8O .

ii) The peak at $m/z = 77$ corresponds to $C_6H_5^+$ ion.

The peak at $m/z = 91$ corresponds to $C_6H_5CH_2^+$ ion.

d)



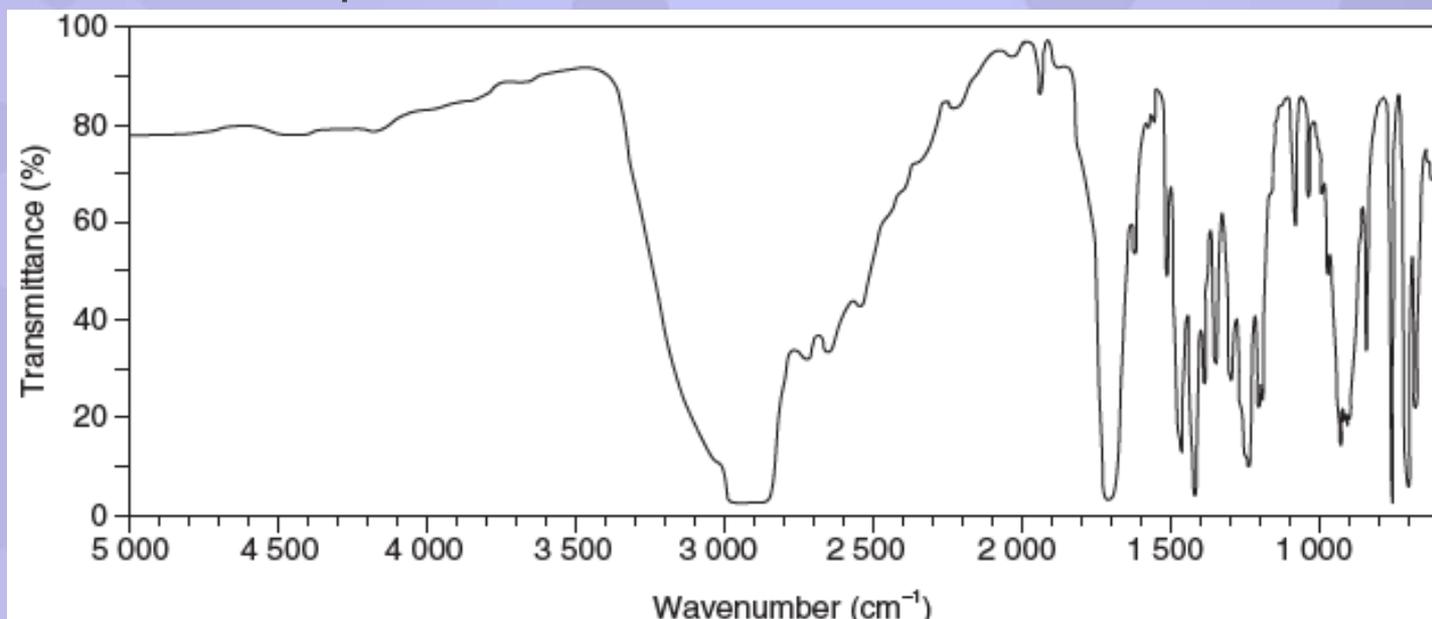


54.14 Identifying unknown carbon compounds by combined techniques (p.157)

Practice 54.6

Compound X contains carbon, hydrogen and oxygen only.

a) The infrared spectrum of X is shown below.



Deduce the functional group(s) that X may have.

(Refer to the information given in Table 54.1.)



54.14 Identifying unknown carbon compounds by combined techniques (p.157)

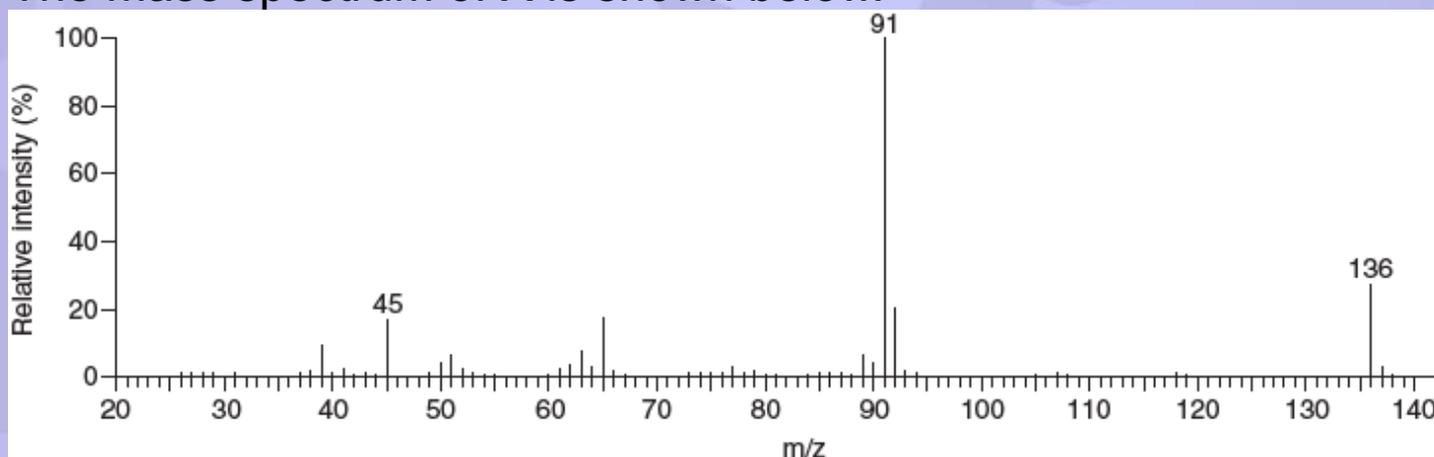
Practice 54.6 (continued)

b) Elemental analysis of X gave the following percentage composition by mass:
carbon 70.6% hydrogen 5.9% oxygen 23.5%

Calculate the empirical formula of X.

(Relative atomic masses: H = 1.0, C = 12.0, O = 16.0)

c) The mass spectrum of X is shown below.



i) Deduce the molecular formula of X.

ii) Suggest ONE chemical species corresponding to each of the signals at m/z = 45 and 91.

d) Draw a possible structure of X.



54.14 Identifying unknown carbon compounds by combined techniques (p.157)

Practice 54.6 (continued)

- a) The broad and strong absorption peak within the range $2\ 500\text{--}3\ 300\ \text{cm}^{-1}$ corresponds to a O–H bond in an acid.
The strong absorption peak at about $1\ 700\ \text{cm}^{-1}$ corresponds to a C=O bond.
Thus, X may contain a –COOH group.
- b) There are 70.6 g of carbon, 5.9 g of hydrogen and 23.5 g of oxygen in 100 g of X.

	Carbon	Hydrogen	Oxygen
Mass of element	70.6 g	5.9 g	23.5 g
Relative atomic mass	12.0	1.0	16.0
Number of moles of atoms	$\frac{70.6\ \text{g}}{12.0\ \text{g mol}^{-1}} = 5.88\ \text{mol}$	$\frac{5.9\ \text{g}}{1.0\ \text{g mol}^{-1}} = 5.9\ \text{mol}$	$\frac{23.5\ \text{g}}{16.0\ \text{g mol}^{-1}} = 1.47\ \text{mol}$
Mole ratio of atoms	$\frac{5.88\ \text{mol}}{1.47\ \text{mol}} = 4$	$\frac{5.9\ \text{mol}}{1.47\ \text{mol}} = 4$	$\frac{1.47\ \text{mol}}{1.47\ \text{mol}} = 1$

\therefore the empirical formula of X is $\text{C}_4\text{H}_4\text{O}$.



54.14 Identifying unknown carbon compounds by combined techniques (p.157)

Practice 54.6 (continued)

c) i) Let $(C_4H_4O)_n$ be the molecular formula of X.

$$\text{Relative molecular mass of X} = n(4 \times 12.0 + 4 \times 1.0 + 16.0)$$

$$= 68n$$

$$68n = 136$$

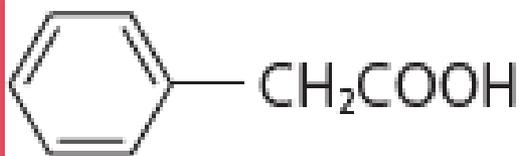
$$n = 2$$

\therefore the molecular formula of X is $C_8H_8O_2$.

ii) The peak at $m/z = 45$ corresponds to $COOH^+$ ion.

The peak at $m/z = 91$ corresponds to $C_6H_5CH_2^+$ ion.

d)





Key terms (p.162)

colorimetry	比色法	wavenumber	波數
infrared spectroscopy	紅外光譜法	fingerprint region	指紋區
mass spectrometry	質譜法	mass spectrometer	質譜儀
complementary colour	互補色	parent peak	母峰
intensity	強度	base peak	基本峰
colorimeter	比色計	fragmentation	碎裂
absorbance	吸光度	fragment ion	碎塊離子
calibration curve	校準曲線	fragmentation pattern	碎裂模式
transmittance	透光率		

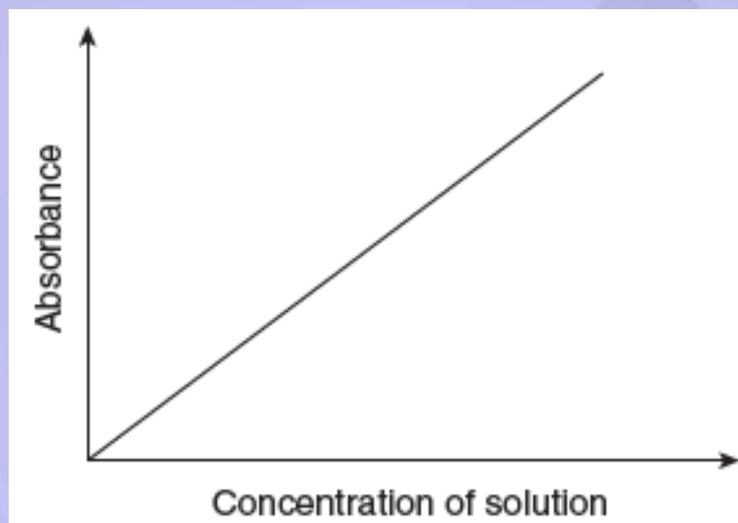


Summary (p.163)

- 1 Compared with traditional analytical methods such as volumetric analysis, instrumental analytical methods have several advantages, including
 - fast;
 - increased level of accuracy;
 - increased level of sensitivity.
- 2 a) Colorimetry is a technique for determining the concentration of a chemical species in solution based on its ability to absorb certain parts of the radiation of the visible spectrum.

 Summary (p.163)

2 b) A calibration curve is prepared by plotting the absorbances of a series of standard solutions against their corresponding concentrations.



Use this graph to determine the concentration of an unknown sample from its absorbance.

 Summary (p.163)

- 3 a) In infrared (IR) spectroscopy, infrared radiation is passed through a sample and the absorptions made by each type of bond in the compound is measured. This produces an infrared spectrum.
- b) There are two main uses for infrared spectra:
- to identify the functional groups present in molecules of carbon compounds;
 - to identify carbon compounds (since each compound has a unique infrared spectrum).



Summary (p.163)

- 4 a) Mass spectrometry can provide information on relative atomic masses of elements, and relative molecular masses and structures of carbon compounds.
- b) Mass spectrometry is a form of analysis that separates and identifies substances on the basis of mass-to-charge ratios of positive ions formed from substances when they are bombarded by high energy electrons in a vacuum.
- c) Structural information of a compound can be determined from fragmentation patterns of the molecular ion. The following table shows typical fragment ions produced in a mass spectrometer and their corresponding m/z values.

Ion	Mass-to-charge ratio (m/z)	Ion	Mass-to-charge ratio (m/z)
CH_3^+	15	C_4H_9^+	57
C_2H_5^+	29	$\text{CH}_3\text{CH}_2\text{CO}^+$	57
CH_3CO^+	43	C_6H_5^+	77
C_3H_7^+	43	$\text{C}_6\text{H}_5\text{CH}_2^+$	91



Unit Exercise (p.165)

Note: Questions are rated according to ascending level of difficulty (from 1 to 5):



question targeted at level 3 and above;



question targeted at level 4 and above;



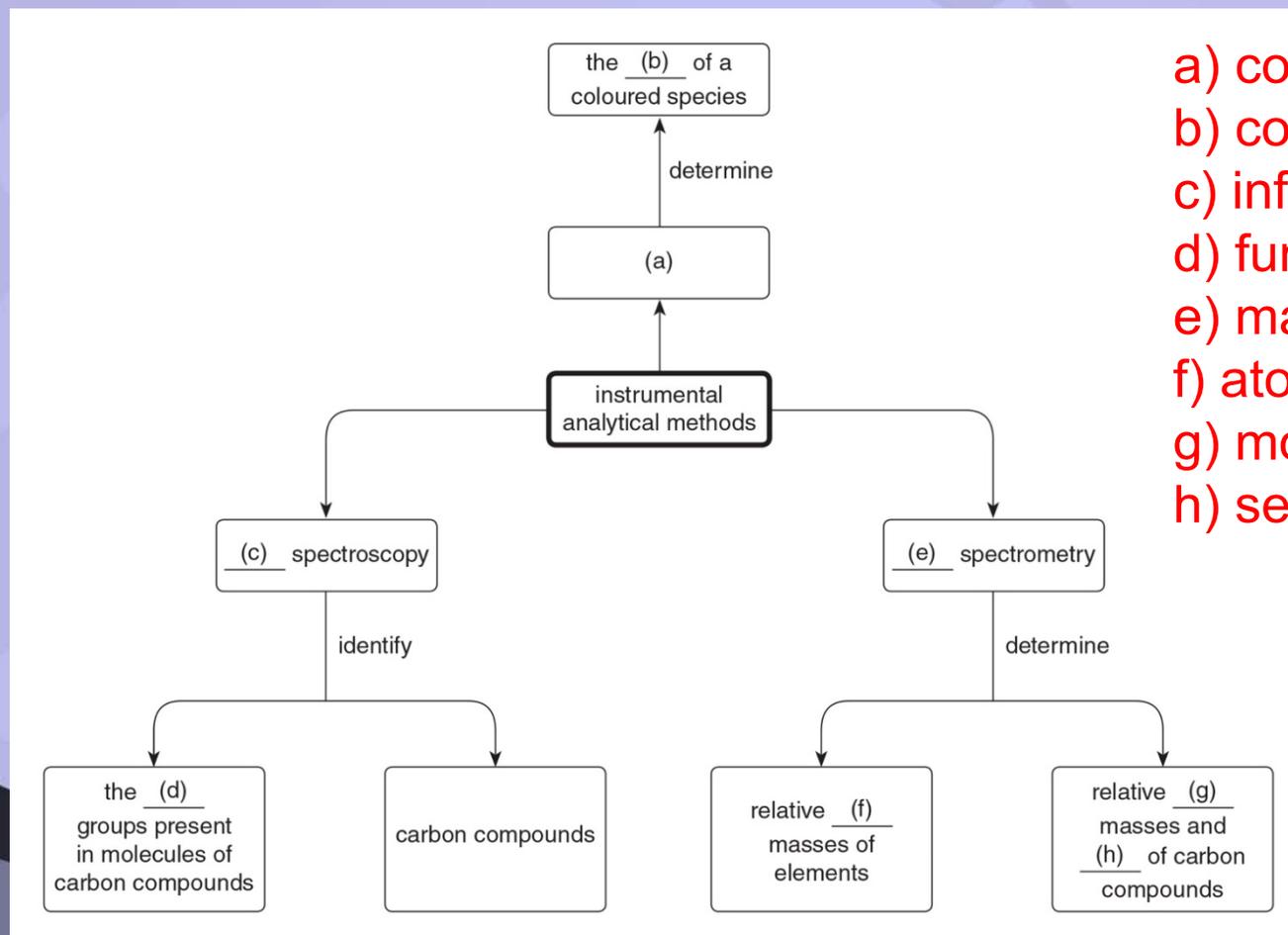
question targeted at level 5.



Unit Exercise (p.165)

PART I KNOWLEDGE AND UNDERSTANDING

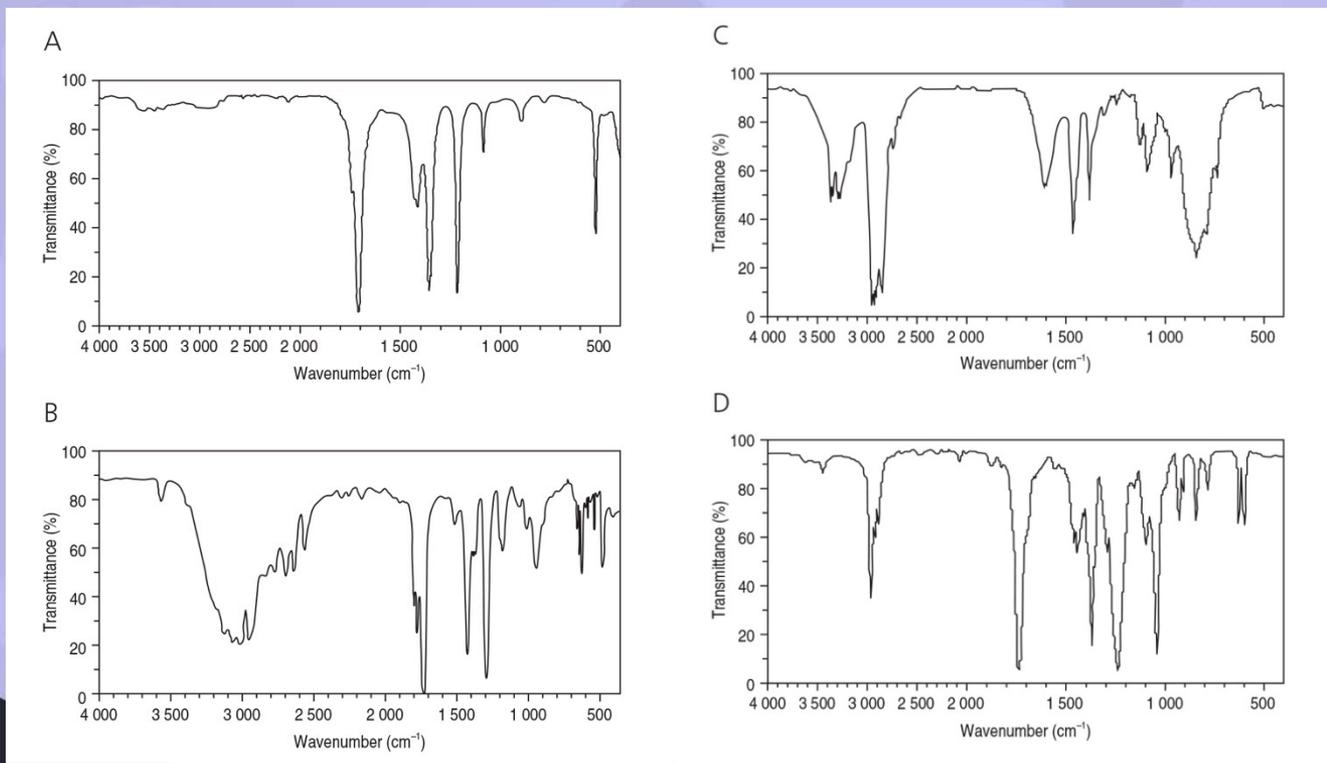
1 Complete the the following concept maps.



- a) colorimetry
- b) concentration
- c) infrared
- d) functional
- e) mass
- f) atomic
- g) molecular
- h) sections of molecules

 Unit Exercise (p.165)**PART II MULTIPLE CHOICE QUESTIONS**

2 Which of the following is the infrared spectrum of an amine?
(Refer to the information given in Table 54.1.)



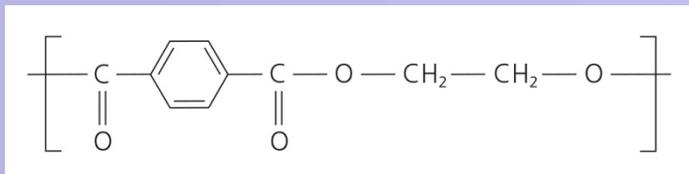
Explanation:
The absorption peak at about 3 350–3 500 cm⁻¹ shows the presence of a N–H bond.

Answer: C



Unit Exercise (p.165)

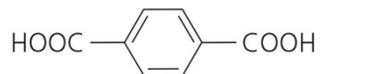
3 PET is a synthetic polymer with the repeating unit shown below.

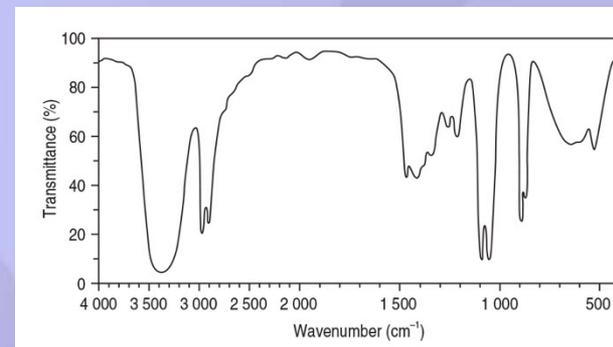


In an experiment, PET is heated under reflux with excess NaOH(aq). The organic products formed are analysed using infrared spectroscopy.

One of the infrared spectra obtained is shown on the right.

What is the structure of this organic product?
(Refer to the information given in Table 54.1.)

- A 
- B 
- C HOCH₂CH₂OH
- D ⁺Na⁻OCH₂CH₂O⁻Na⁺



Explanation:

The broad and strong absorption peak at about 3 230–3 670 cm⁻¹ shows the presence of O–H bonds (alcohols).

Answer: C

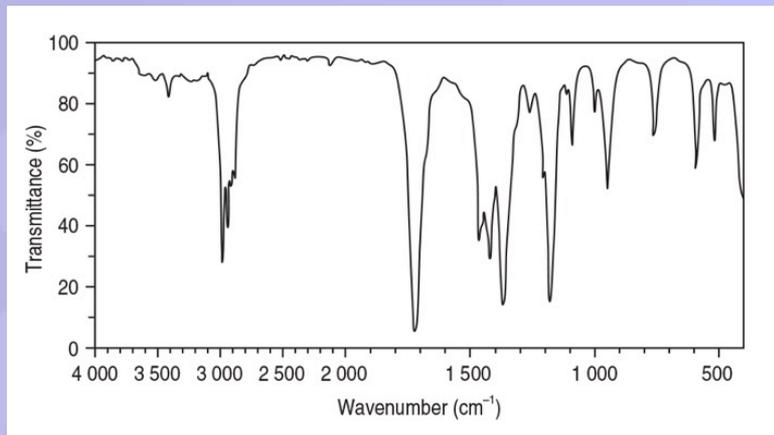


Key terms (p.162)

4 An alcohol A is heated under reflux with sulphuric acid and potassium dichromate.



The organic compound formed produces the infrared spectrum below.



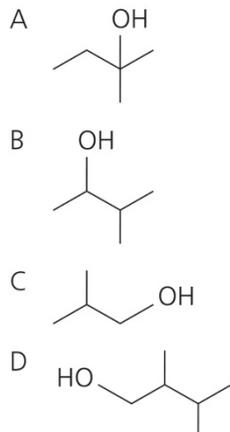
Explanation:

The infrared spectrum of the oxidation product has an absorption peak at about $1\ 680\text{--}1\ 800\ \text{cm}^{-1}$, which corresponds to a C=O bond.

The spectrum does not show an absorption peak at about $2\ 500\text{--}3\ 300\ \text{cm}^{-1}$, ruling out the presence of a O-H bond in an acid.

It can be deduced that the oxidation product is a ketone. Alcohol A should be a secondary alcohol.

Which compound could be alcohol A?



Answer: B

(OCR Advanced Subsidiary, Chem. A, H032/01, Jun. 2017, 19)

 Unit Exercise (p.165)

5 Consider the ester shown below.



Which of the following chemical species produces the parent peak in the mass spectrum of this ester?

- A $[\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3]^+$
- B $[\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3]^{2+}$
- C $[\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3]^-$
- D $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$

Answer: A



Unit Exercise (p.165)

- 6  The mass spectrum of a compound, Z, has a peak at $m/z = 43$. Which of the following could NOT be Z?

(Relative atomic masses: H = 1.0, C = 12.0, O = 16.0)

- A $\text{CH}_3\text{COCH}_2\text{CH}_3$
- B $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$
- C $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3$
- D $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$

Explanation:

(Edexcel IAL, Advanced, Unit 5, Jun. 2014, 16)

The mass spectra of $\text{CH}_3\text{COCH}_2\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3$ have a peak at $m/z = 43$.

Answer: D

Mass spectrum of	Chemical species corresponding to peak at $m/z = 43$
$\text{CH}_3\text{COCH}_2\text{CH}_3$	CH_3CO^+
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	$\text{CH}_3\text{CH}_2\text{CH}_2^+$ or CH_2CHO^+
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3$	$\text{CH}_3\text{CH}_2\text{CH}_2^+$ or CH_3CO^+



 Unit Exercise (p.165)

7 Which of the following statements concerning a mass spectrum of a carbon compound is / are correct?

(1) It enables the relative molecular mass of the compound to be determined.

(2) The unit of the x-axis is 'mass'.

(3) The units of the y-axis are 'percentage of transmittance'. **Explanation:**

(2) The units of the x-axis are mass-to-charge ratio (m/z).

(3) The units of the y-axis are 'relative intensity'.

A (1) only

B (2) only

C (1) and (3) only

D (2) and (3) only

Answer: A

 Unit Exercise (p.165)

9 Which of the following analytical methods are based on the measurement of absorption of electromagnetic radiation?

- (1) Colorimetry
- (2) Infrared spectroscopy
- (3) Mass spectrometry

- A (1) and (2) only
- B (1) and (3) only
- C (2) and (3) only
- D (1), (2) and (3)

Answer: A

 Unit Exercise (p.165)

10 Propanal ($\text{CH}_3\text{CH}_2\text{CHO}$) and propanone (CH_3COCH_3) are compared using instrumental methods. Which of the following comparisons are correct?

- (1) They have different patterns in the fingerprint regions of their infrared spectra.
- (2) They have different fragmentation patterns in their mass spectra.
- (3) They have parent peaks with different m/z values in their mass spectra.

Answer: A

Explanation:

- A (1) and (2) only (3) $\text{CH}_3\text{CH}_2\text{CHO}$ and CH_3COCH_3 has the same relative molecular mass. Their spectra have parent peaks at the same m/z value.
- B (1) and (3) only
- C (2) and (3) only
- D (1), (2) and (3)

 Unit Exercise (p.165)**PART III STRUCTURED QUESTIONS**

11 Chemical analysis can be used to find out whether a coin is genuine or fake.

- a) It is possible to prove that the coin is genuine by identifying the elements in the coin. **Mass spectrometry (1)**
Name an instrumental method of analysis that could be used to identify the elements in the coin.
- b) Give TWO reasons for using instrumental methods for analysis.

Any two of the following:

- **Fast / quick (1)**
- **Can detect small amounts of samples / sensitive (1)**
- **Accurate (1)**
- **Reliable / efficient (1)**



Unit Exercise (p.165)



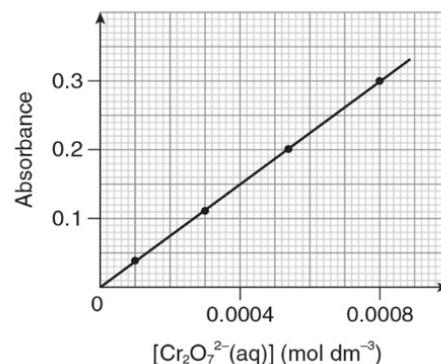
12 The concentration of a $\text{Na}_2\text{Cr}_2\text{O}_7(\text{aq})$ sample A was determined by volumetric analysis; while the concentration of another $\text{Na}_2\text{Cr}_2\text{O}_7(\text{aq})$ sample B was determined by colorimetry.

a) 25.00 cm^3 of sample A was transferred to a conical flask and acidified with dilute $\text{H}_2\text{SO}_4(\text{aq})$. Then the mixture was titrated with $0.0642 \text{ mol dm}^{-3} \text{ Fe}^{2+}(\text{aq})$ solution with a suitable indicator. It required 26.88 cm^3 of the $\text{Fe}^{2+}(\text{aq})$ solution to reach the end point.

i) Write a balanced equation for the reaction involved.

ii) Calculate the concentration of $\text{Na}_2\text{Cr}_2\text{O}_7(\text{aq})$ in A.

b) In colorimetry, various standard $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ solutions were first prepared, and then the absorbance of these solutions were measured with a colorimeter installed with a blue filter. The calibration curve below shows the variation of absorbance with the concentration of $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ ions.





Unit Exercise (p.165)

12 [\(continued\)](#)



b) i) Suggest why a blue filter was used.

ii) With reference to the above calibration curve, state the relationship between absorbance and $[\text{Cr}_2\text{O}_7^{2-}(\text{aq})]$.

iii) Sample B was diluted 100 times. The absorbance of the diluted solution was measured as 0.26 by the colorimeter. Based on the information given from the above calibration curve, calculate the concentration of $\text{Na}_2\text{Cr}_2\text{O}_7(\text{aq})$ in B.

c) Explain whether volumetric analysis or colorimetry is more appropriate in determining the concentration of a very dilute $\text{Na}_2\text{Cr}_2\text{O}_7(\text{aq})$, such as around $10^{-4} \text{ mol dm}^{-3}$.

(HKDSE, Paper 2, 2016, 3(b))

Answers for the questions of the public examinations in Hong Kong are not provided (if applicable).



Unit Exercise (p.165)

13 There are four isomeric alcohols with the molecular formula $C_4H_{10}O$.

a) Isomers W and X are both straight-chain alcohols.

W can be oxidised to form P.

X can be oxidised to form Q.

P and Q are isomers with molecular formula C_4H_8O . When tested with Tollens' reagent,

P gives a negative result while Q gives a positive result.

Use the information above about compounds P and Q to identify alcohols W and X.

Explain your answer with reference to the functional groups in P and Q.

Q is an aldehyde while P is a ketone. (1)

W is a straight-chain secondary alcohol, i.e. butan-2-ol. It gives a ketone upon oxidation. (1)

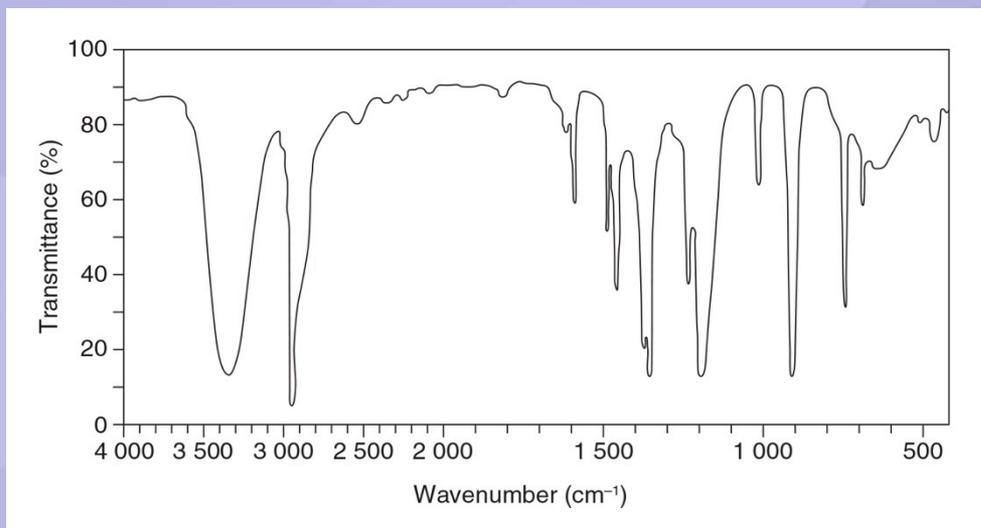
X is a straight-chain primary alcohol, i.e. butan-1-ol. It gives an aldehyde upon oxidation. (1)



Unit Exercise (p.165)

13 [\(continued\)](#)

b) The infrared spectrum of one of the four isomeric alcohols is shown below.



i) Identify ONE feature of the infrared spectrum which supports the fact that this is an alcohol.

(Refer to the information given in Table 54.1.)

The absorption peak in the range of 3 230–3 670 cm⁻¹ supports the presence of a O–H bond (alcohol). (1)

ii) Explain how infrared spectroscopy can be used to identify this isomeric alcohol.

Match the fingerprint region of the spectrum with spectra of known samples / database spectra. (1)

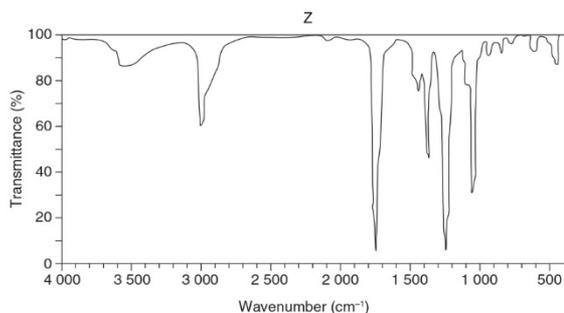
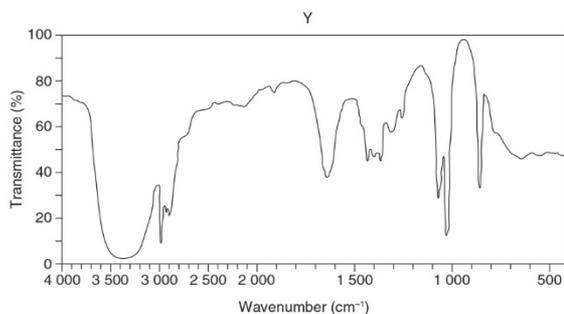
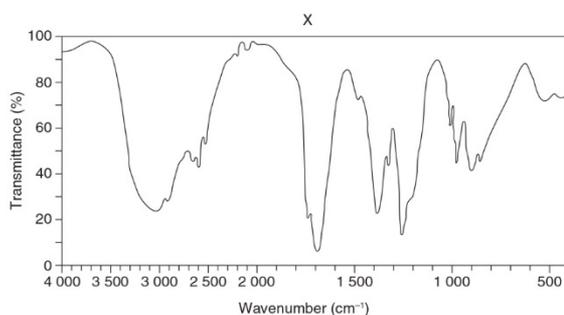


Unit Exercise (p.165)

14



The infrared spectra of three compounds X, Y and Z are shown below. The compounds are an ester, a carboxylic acid and an alcohol, though not necessarily in that order.



- a) Identify the key peaks in each spectrum, and the bond to which each corresponds.

(Refer to the information given in Table 54.1.)

Spectrum X

The broad and strong absorption peak at about $2\,500\text{--}3\,300\text{ cm}^{-1}$ corresponds to a O–H bond (acid). (1)
The strong absorption peak at about $1\,680\text{--}1\,800\text{ cm}^{-1}$ corresponds to a C=O bond.

Spectrum Y

The broad and strong absorption peak at about $3\,230\text{--}3\,670\text{ cm}^{-1}$ corresponds to a O–H bond (alcohol). (1)

Spectrum Z

The broad and strong absorption peak at about $1\,680\text{--}1\,800\text{ cm}^{-1}$ corresponds to a C=O bond. (1)

- b) Decide which spectrum represents which compound.

X — a carboxylic acid

Y — an alcohol

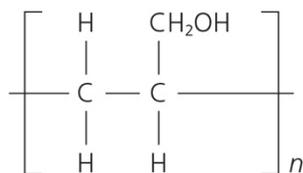
Z — an ester

(1)



Unit Exercise (p.165)

15 a) Compound X is an isomer of propanal. It can be polymerised to form a polymer with the structure shown below.



i) Draw the structure of X.



ii) Give the systematic name of X.



iii) There are two functional groups in X. Each of these functional groups contains a bond with a characteristic absorption range in the infrared spectrum.

Suggest a bond and its absorption range for each of the two functional groups.

(Refer to the information given in Table 54.1.)





Unit Exercise (p.165)

15 [\(continued\)](#)

b) Compound Y is another isomer of propanal. The infrared spectrum of Y shows an absorption in the range 1 680–1 750 cm^{-1} .

i) Draw the structure of Y.



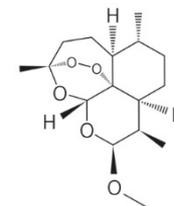
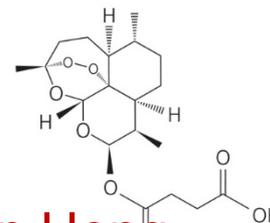
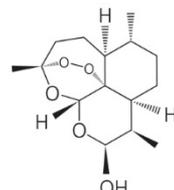
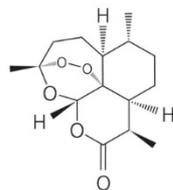
ii) Propanal and Y are structural isomers. Name the type of isomerism shown.

Functional group isomerism (1)



Unit Exercise (p.165)

16 Artemisinin is an organic compound obtained from a certain plant. Artemisinin cannot react with $\text{NaHCO}_3(\text{aq})$. Its infrared spectrum shows a strong absorption peak at around 1700 cm^{-1} . Suggest which one of W, X, Y and Z below would be a possible structure of artemisinin. Explain your answer.



Answers for the questions of the public examinations in Hong Kong are not provided (if applicable).

Characteristic infrared absorption wavenumber ranges
(stretching modes)

Bond	Compound type	Wavenumber range (cm^{-1})
C=C	alkenes	1 610–1 680
C=O	aldehydes, ketones, carboxylic acids and derivatives	1 680–1 800
C≡C	alkynes	2 070–2 250
C≡N	nitriles	2 200–2 280
O–H	acids (hydrogen-bonded)	2 500–3 300
C–H	alkanes, alkenes, arenes	2 840–3 095
O–H	alcohols (hydrogen-bonded)	3 230–3 670
N–H	amines	3 350–3 500

(Relative atomic masses: H = 1.0, N = 14.0, O = 16.0)

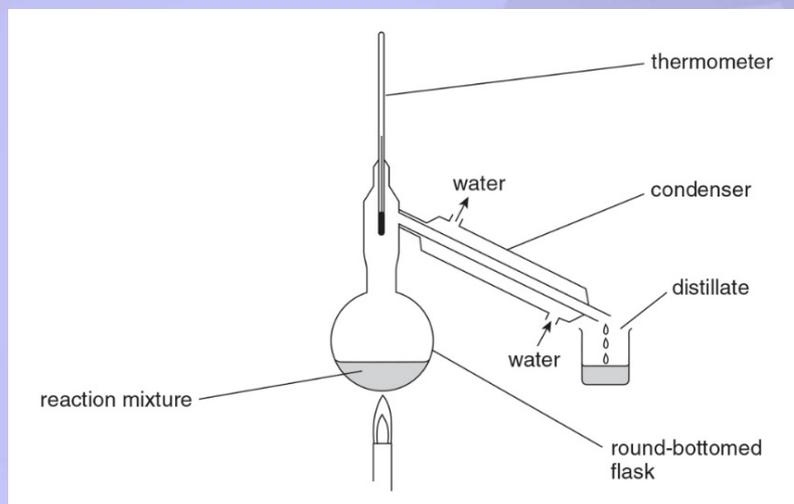
(HKDSE, Paper 2, 2017, 3(c)(ii))



Unit Exercise (p.165)

17  Ethane-1,2-diol, $\text{CH}_2\text{OHCH}_2\text{OH}$, is commonly used in antifreeze for cars to lower the freezing temperature of the water in the car radiator. It reacts in a similar way to ethanol but both of the alcohol groups can react.

a) Ethane-1,2-diol is very quickly oxidised to ethanedioic acid, $(\text{COOH})_2$, even under the conditions shown below.



However, ethanol requires stronger oxidising conditions to be converted into ethanoic acid.

Explain how you would change the above apparatus to achieve this oxidation of ethanol.

Remove the thermometer / still head / leave the top of the condenser open. (1)

Place the condenser directly on top of the flask / in vertical position. (1)

 Unit Exercise (p.165)17 [\(continued\)](#)

b) Mass spectrometry can be used to identify the products of the oxidation of ethanol. Suggest the formula of a fragment that would show when ethanoic acid is produced and would NOT be present in either ethanol or ethanal.

(Edexcel Advanced Subsidiary GCE, Unit 2, 6CH02/01R, Jun. 2013, 22(b), (e)(iii))

Any one of the following:

- COOH^+ (1)
- CH_3COO^+ (1)
- CH_3COOH^+ (1)

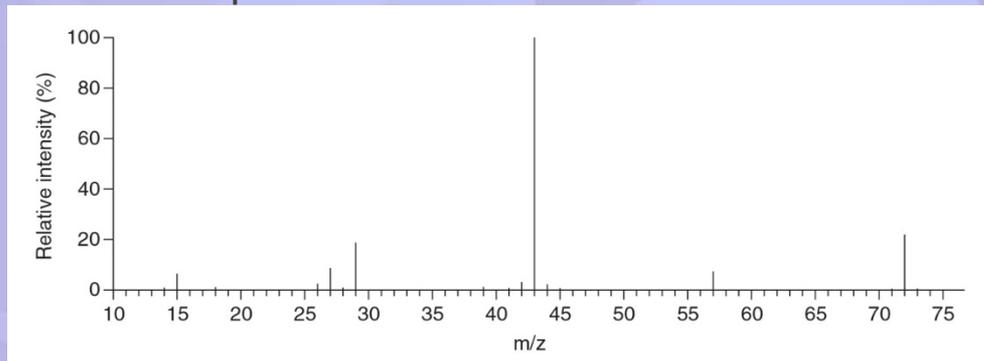


Unit Exercise (p.165)

18 Compound X gives a positive result when tested with 2,4-dinitrophenylhydrazine, but gives a negative result with Tollens' reagent.



- What is the purpose of using 2,4-dinitrophenylhydrazine.
Test for aldehyde group or ketone group (1)
- State the expected observation when X is tested with 2,4-dinitrophenylhydrazine.
A bright red / orange / yellow precipitate (1)
- With reference to the test results of 2,4-dinitrophenylhydrazine and Tollens' reagent, suggest ONE functional group that may be present in X.
A ketone group (1)
- The mass spectrum of X is shown below.



Suggest one chemical species corresponding to the signal at $m/z = 43$.





Unit Exercise (p.165)

18 [\(continued\)](#)



e) Identify X.

The relative molecular mass of X is 72.

X is probably butanone. (1)

f) Compound Y has the same relative molecular mass as X. The infrared spectrum of Y contains a broad absorption between 2 500–3 300 cm^{-1} as well as an absorption between 1 680–1 750 cm^{-1} .

Identify Y. Explain your reasoning.

(Refer to the information given in Table 54.1.)

The absorption between 2 500–3 300 cm^{-1} corresponds to a O–H group (acid). (1)

The absorption between 1 680–1 750 cm^{-1} corresponds to a C=O bond. (1)

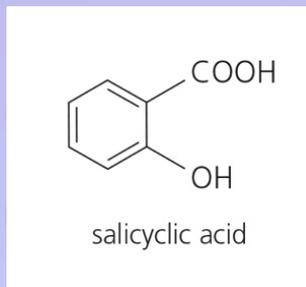
Y is $\text{CH}_2=\text{CHCOOH}$. (1)



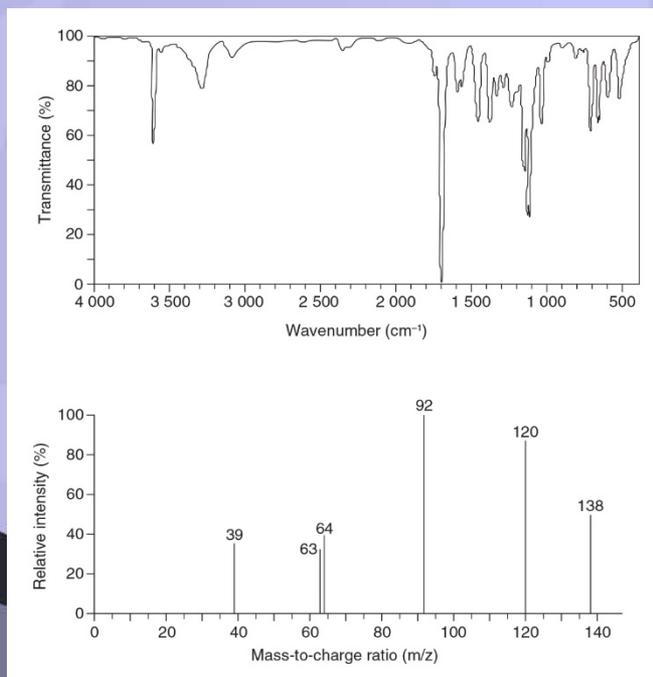
Unit Exercise (p.165)



- 19 The bark and leaves of the willow tree have long been used to relieve fevers and pain. The active ingredient in willow extract is salicylic acid.



The infrared spectrum and mass spectrum of salicylic acid are shown below.



- a) Identify the bonds responsible for the main infrared absorptions.

(Refer to the information given in Table 54.1.)

Infrared absorption	Bond
3 600 cm ⁻¹	O-H (alcohol) (1)
3 200 cm ⁻¹	O-H (acid) (1)
1 700 cm ⁻¹	C=O (1)



Unit Exercise (p.165)

19 [\(continued\)](#)



b) Explain what is happening inside the salicylic acid molecule when infrared radiation is being absorbed.

The bonds in salicylic acid absorb energy from infrared radiation of certain frequencies and vibrate more. (1)

c) Consider the mass spectrum of salicylic acid.

i) Identify the parent peak.

138 (1)

ii) Suggest one chemical species corresponding to the signal at $m/z = 120$.

$C_6H_4COO^+$ (1)

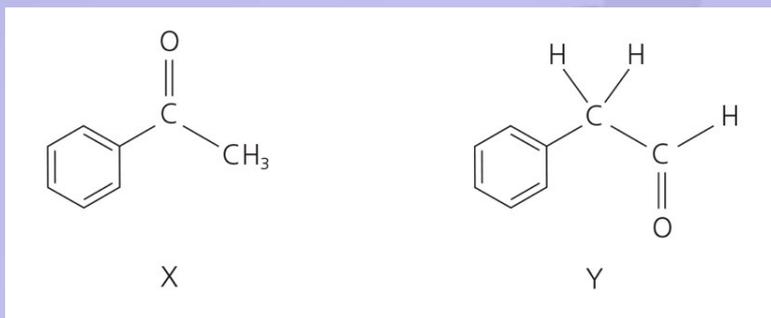
(Relative atomic masses: H = 1.0, C = 12.0, O = 16.0)



Unit Exercise (p.165)

Answers for the questions of the public examinations in Hong Kong are not provided (if applicable).

20 Compounds X and Y shown below are isomers with relative molecular mass 120.



- Each of X and Y can react with 2,4-dinitrophenylhydrazine solution to give a similar observation. State the observation.
- Suggest a chemical test to distinguish between X and Y.
- Illustrate how X and Y can be distinguished from their mass spectra.
- With reference to the information given in the table below, suggest whether infrared spectroscopy can be used to distinguish between X and Y.

Characteristic infrared absorption wavenumber ranges
(stretching modes)

Bond	Compound type	Wavenumber range (cm ⁻¹)
C=C	alkenes	1 610–1 680
C=O	aldehydes, ketones, carboxylic acids and derivatives	1 680–1 800
C≡C	alkynes	2 070–2 250
C≡N	nitriles	2 200–2 280
O–H	acids (hydrogen-bonded)	2 500–3 300
C–H	alkanes, alkenes, arenes	2 840–3 095
O–H	alcohols, phenols (hydrogen-bonded)	3 230–3 670
N–H	amines	3 350–3 500

(HKDSE, Paper 2, 2015, 3(b))

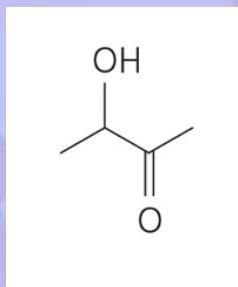
(HKDSE, Paper 2, 2015, 3(b))



Unit Exercise (p.165)



21 Acetoin is found naturally in butter and is added to foods to give a buttery taste. It is also added to some cigarettes to improve flavour. The structure of acetoin is shown below.

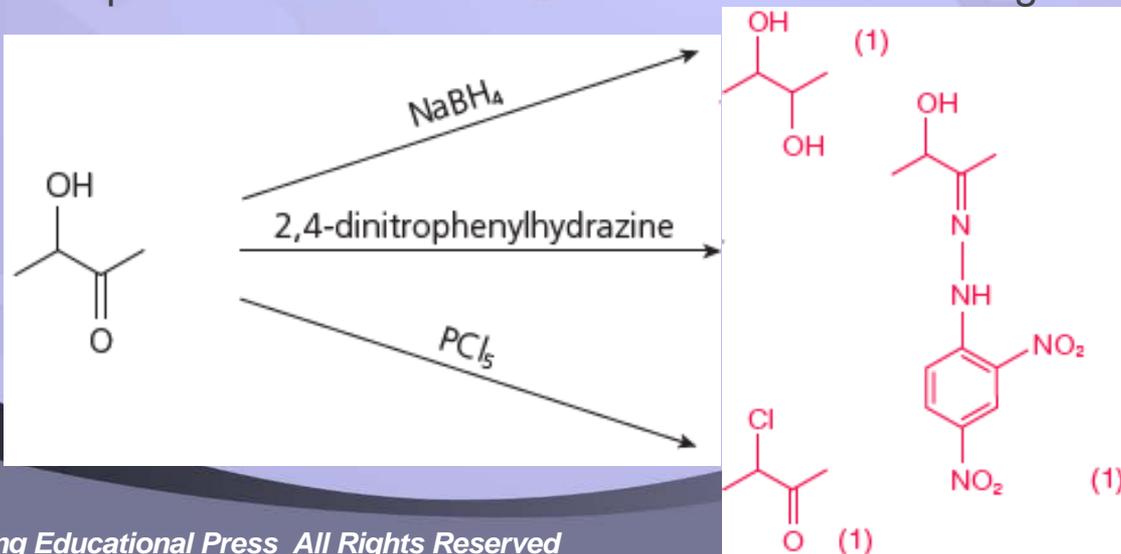


a) i) Explain why acetoin is soluble in water.

Acetoin molecules can form hydrogen bonds with water molecules. (1)

ii) The scheme below shows some of the reactions of acetoin.

Complete the scheme to show the structure of the organic product for each reaction.



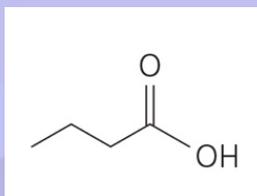


Unit Exercise (p.165)

21 (continued)



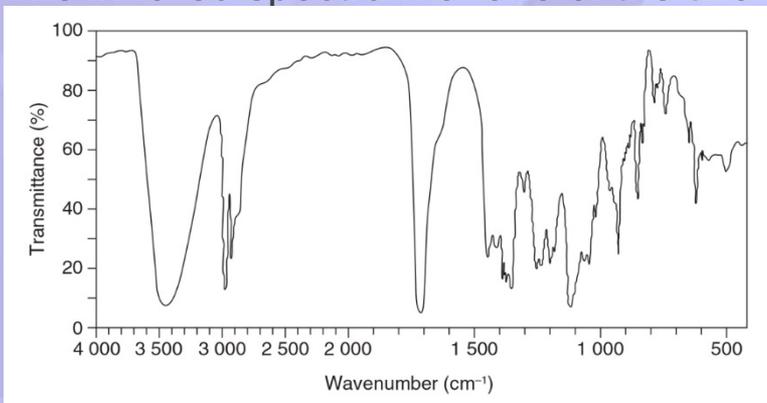
b) Compound X is an isomer of acetoin.



i) Identify an ion which could cause a peak in the mass spectrum of X but NOT of acetoin.

$\text{CH}_3\text{CH}_2\text{CH}_2^+$ / CH_3CH_2^+ / CH_2^+ / COOH^+ / COO^+ (1)

ii) The infrared spectrum of one of the two isomers is shown below.



Acetoin

The absorption peak at about $3\ 230\text{--}3\ 670\ \text{cm}^{-1}$ corresponds to a O-H bond (alcohol). (1)

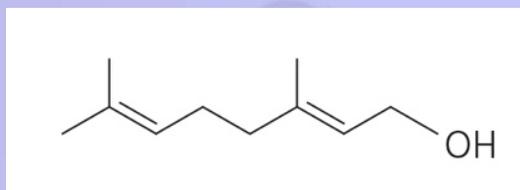
Identify the isomer. Explain your reasoning.
(Refer to the information given in Table 54.1.)



Unit Exercise (p.165)



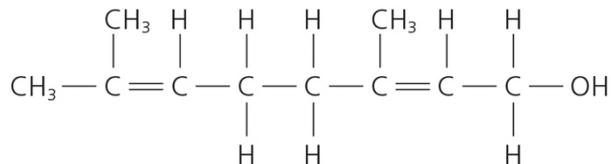
- 22 a) The characteristic smell of pine wood is due, partly, to the presence of a group of compounds called terpenes. One of the simpler terpenes is a compound called geraniol, which is an oily liquid at room temperature and pressure. The structure of geraniol is



Deduce the molecular formula of geraniol. Use your answer to calculate the molar mass of geraniol in g mol^{-1} .

(Relative atomic masses: $\text{H} = 1.0$, $\text{C} = 12.0$, $\text{O} = 16.0$)

The structure of geraniol is:



The molecular formula of geraniol is $\text{C}_{10}\text{H}_{18}\text{O}$. (1)

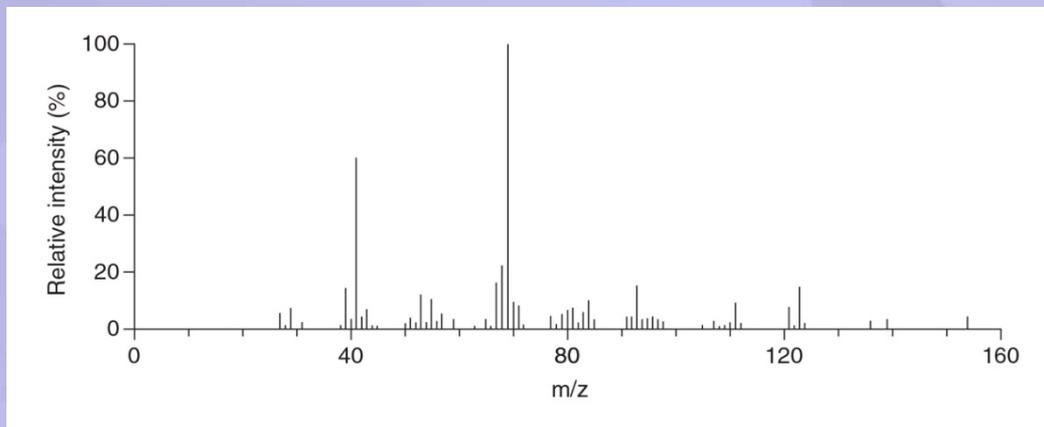
Molar mass of geraniol = $(10 \times 12.0 + 18 \times 1.0 + 16.0) \text{ g mol}^{-1}$
 $= 154.0 \text{ g mol}^{-1}$ (1)



Unit Exercise (p.165)

22 [\(continued\)](#)

 b) The mass spectrum of geraniol is shown.



i) Show that this mass spectrum can be used to confirm the molar mass of geraniol.

The furthest peak to right has a m/z value equals to 154. /

The highest m/z value is 154. (1)

ii) Identify an ion that could be responsible for the peak at m/z = 69.

$C_5H_9^+$ (1)

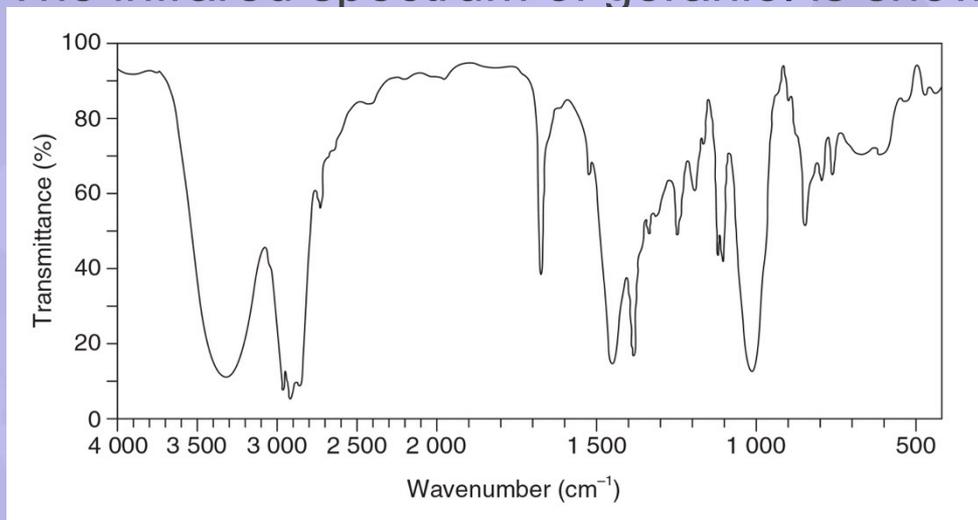


Unit Exercise (p.165)

22 [\(continued\)](#)



c) The infrared spectrum of geraniol is shown.



Using Table 54.1 and the infrared spectrum, give the NAMES of the two functional groups present in geraniol. To confirm these functional groups, give the wavenumber

Functional group	Wavenumber range
Carbon-carbon double bond	1 610–1 680
O–H bond (alcohol)	3 230–3 670

(1)

(1)



Unit Exercise (p.165)

22 [\(continued\)](#)



d) Give ONE chemical test that you could use to confirm the presence of each of the two functional groups suggested in part (c). Predict a result for each test.

(Edexcel Advanced Subsidiary GCE, Paper 2, Jun. 2017, 4(a)–(d))

Carbon-carbon double bond

Add aqueous bromine to geraniol slowly. (1)

Aqueous bromine changes from yellow-brown to colourless quickly. (1)

Hydroxyl group

Mix geraniol with phosphorus pentachloride. (1)

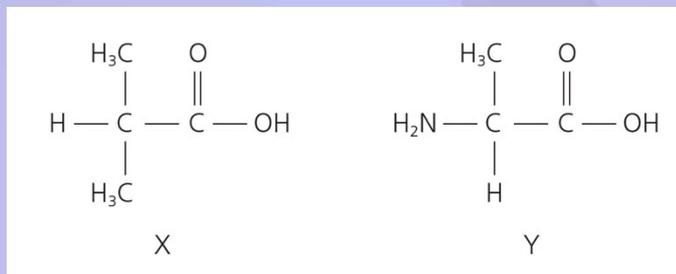
White fumes would be observed. (1)



Unit Exercise (p.165)



23 Spectroscopic techniques can be used to distinguish between compounds X and Y, shown below.



Suggest how compounds X and Y can be differentiated from their respective

- a) infrared spectra;
- b) mass spectra.

(Relative atomic masses: H = 1.0, C = 12.0, N = 14.0, O = 16.0)

(Refer to the information given in Table 54.1.)



Unit Exercise (p.165)

23 (continued)



- a) Only the infrared spectrum of Y has absorption peak at $3\ 350\text{--}3\ 500\ \text{cm}^{-1}$ corresponding to a N–H bond. (1)
The two infrared spectra have different fingerprint regions. (1)
- b) The mass spectra of the two compounds have different parent peaks (X has parent peak at $m/z = 88$ while Y has parent peak at $m/z = 89$). (1)
The two compounds have different fragmentation patterns.
Spectrum of X has the following peaks:

m/z value	Corresponding chemical species	
71	$(\text{CH}_3)_2\text{CHCO}^+$	(1)
43	$\text{CH}_3\text{CHCH}_3^+$	(1)

Spectrum of Y has the following peaks (any two of the following):

m/z value	Corresponding chemical species	
72	$\text{CH}_3(\text{NH}_2)\text{CHCO}^+$	(1)
44	$\text{H}_2\text{NCHCH}_3^+$	(1)
29	H_2NCH^+	(1)
16	NH_2^+	(1)

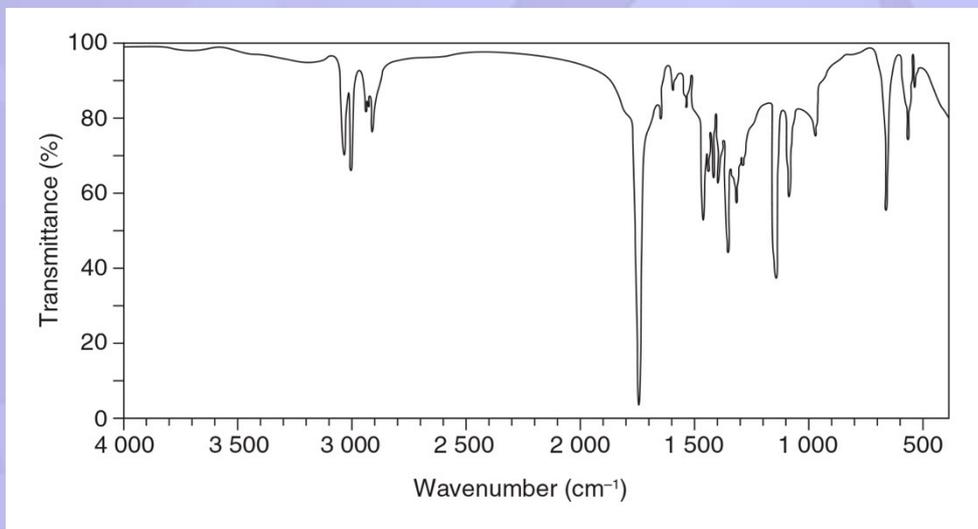


Unit Exercise (p.165)



24 Under room temperature, T ($C_xH_yO_z$) is a colourless oily liquid and is immiscible with water. Moreover, T does not react with $NaHCO_3(aq)$.

- a) With reference to the information given below, deduce the functional group(s) that T may have.
- i) T is NOT an ester, and it gives negative result with Tollens' reagent.
- ii) T gives the following infrared spectrum:





Unit Exercise (p.165)

24 (continued)

Characteristic infrared absorption wavenumber ranges
(stretching modes)

Bond	Compound type	Wavenumber range (cm ⁻¹)
C=C	alkenes	1 610–1 680
C=O	aldehydes, ketones, carboxylic acids and derivatives	1 680–1 800
C≡C	alkynes	2 070–2 250
C≡N	nitriles	2 200–2 280
O–H	acids (hydrogen-bonded)	2 500–3 300
C–H	alkanes, alkenes, arenes	2 840–3 095
O–H	alcohols, phenols (hydrogen-bonded)	3 230–3 670
N–H	amines	3 350–3 500

- b) The mass spectrum of T shows a parent peak at $m/z = 134$, and a strong peak at each of $m/z = 43$ and 91 . Suggest ONE chemical species corresponding to each of the signals at $m/z = 43$ and 134 .
- c) Draw ONE possible structure of T.

(HKDSE, Paper 2, 2014, 3(c)(ii)–(iv))

Answers for the questions of the public examinations in Hong Kong are not provided (if applicable).