

Chapter 15

Modern analytical techniques

Testing drivers

In [Chapter 13](#) you saw how ethanol is the alcohol found in all alcoholic drinks and how some people abuse this substance. ‘Drink driving’ is a major factor in many fatal accidents. Innocent people can be killed because the driver of another car is ‘over the limit’. The legal limit for driving in the UK is 80 mg of ethanol per 100 cm³ of blood.

If police suspect a driver has been drinking they conduct a road-side breathalyser test in which the driver blows into a small hand-held device (see [Figure 15.1](#)). This gives the police officer an approximate idea of the alcohol level of the suspect and indicates whether or not they might be over the limit.

A more accurate test is performed at a police station where an infrared spectrometer is used to test the driver’s breath. If the breath sample test is positive, the driver can then opt for a further test on their blood to ensure there is no error.



Figure 15.1 This initial breathalyser test tells the police officer whether a more accurate test using infrared spectroscopy is needed at a police station.

continued

You can see the infrared spectrum of ethanol in [Figure 15.2](#). Infrared radiation passes through a sample of ethanol in the machine, causing the bonds in the ethanol molecule to vibrate (e.g. bend or stretch more vigorously). The ethanol absorbs the infrared radiation when this happens. The troughs in the spectrum correspond to the absorption of different frequencies of infrared radiation by different bonds.

Water in the breath can interfere with the O–H bond absorbance (at 3340 cm⁻¹) but the sharp trough due to a C–H bond (at 2950 cm⁻¹) can be used by a computer to calculate the percentage of ethanol present.

Structural identification using infrared spectroscopy

In a modern infrared spectrometer, a beam of infrared radiation is passed through a sample of the chemical to be identified. Computer analysis enables the absorbance of radiation to be measured at different frequencies. Study of the resulting spectrum enables the presence (or absence) of particular functional groups to be established.

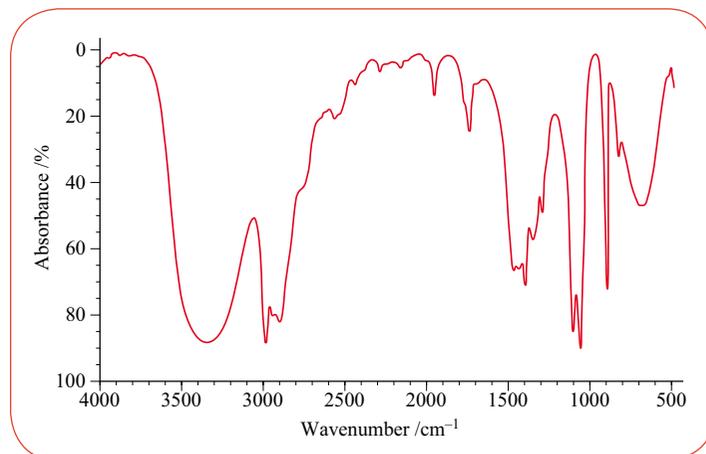


Figure 15.2 The infrared spectrum of ethanol. Notice that absorbance increases in a downward direction.

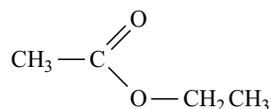
An unusual unit is used to measure frequency, the wavenumber or cm^{-1} . Table 15.1 shows the absorption frequencies which we shall use in this unit.

Functional group	Location	Wave-number / cm^{-1}	Absorbance
O–H	alcohols	3230–3550	strong, broad
O–H	carboxylic acids	2500–3500	medium, very broad
C=O	aldehydes, ketones, acids and esters	1680–1750	strong, sharp

Table 15.1 Infrared absorption frequencies of some functional groups.

Look again at the infrared spectrum of ethanol in Figure 15.2. Most of the absorptions are sharp and some overlap. The absorption of interest is the strong, broad absorption at about 3420 cm^{-1} , which shows the presence of the O–H group. (The O–H absorptions are usually broadened by the effect of hydrogen bonding between molecules.)

If ethanol is warmed with ethanoic acid in the presence of a few drops of concentrated sulfuric acid, ethyl ethanoate (see Chapter 13) is formed:



How do we know that the ester is present? The infrared spectrum of a pure sample of ethyl ethanoate is shown in Figure 15.3.

Note the absence of the strong, broad absorption from the O–H group in ethanol. Instead, there is a strong, sharp absorption at 1720 cm^{-1} which arises from the C=O group.

When ethanol is refluxed with an excess of potassium dichromate and dilute sulfuric acid,

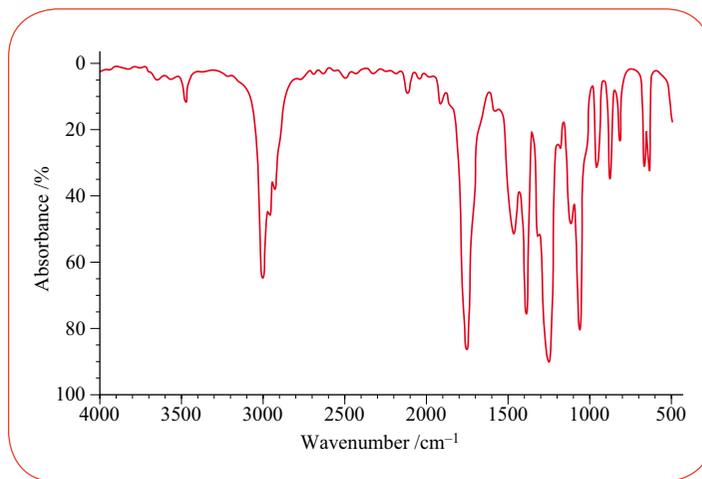


Figure 15.3 The infrared spectrum of ethyl ethanoate.

ethanoic acid is formed (see Chapter 13). Infrared spectroscopy again helps us to distinguish the product from ethanol. The infrared spectrum of a pure sample of ethanoic acid is shown in Figure 15.4.

The strong, very broad absorption between 2500 and 3500 cm^{-1} is partly due to the O–H group in the acid. (Although groups containing C–H bonds also absorb in this region, they are of little help in identification as such bonds are present in all organic compounds.) Compare the spectrum of ethanoic acid with that of ethanol. There are clear differences between the two spectra.

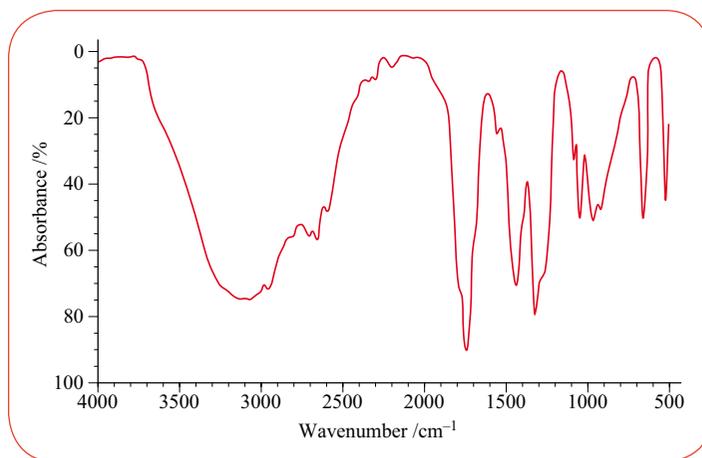


Figure 15.4 The infrared spectrum of ethanoic acid.

SAQ

- 1 a Draw the structural formula of ethanoic acid.
- b Apart from the O–H group, which other group can be identified in the spectrum for ethanoic acid? Use Figure 15.4 to record the absorbance and frequency of this bond.

- Oxidation of a primary alcohol under milder conditions produces an aldehyde, for example ethanal, CH_3CHO , from ethanol, $\text{C}_2\text{H}_5\text{OH}$.
- Oxidation of secondary alcohols produces ketones, for example propanone, CH_3COCH_3 , from propan-2-ol, $\text{CH}_3\text{CHOHCH}_3$ (see Chapter 13).

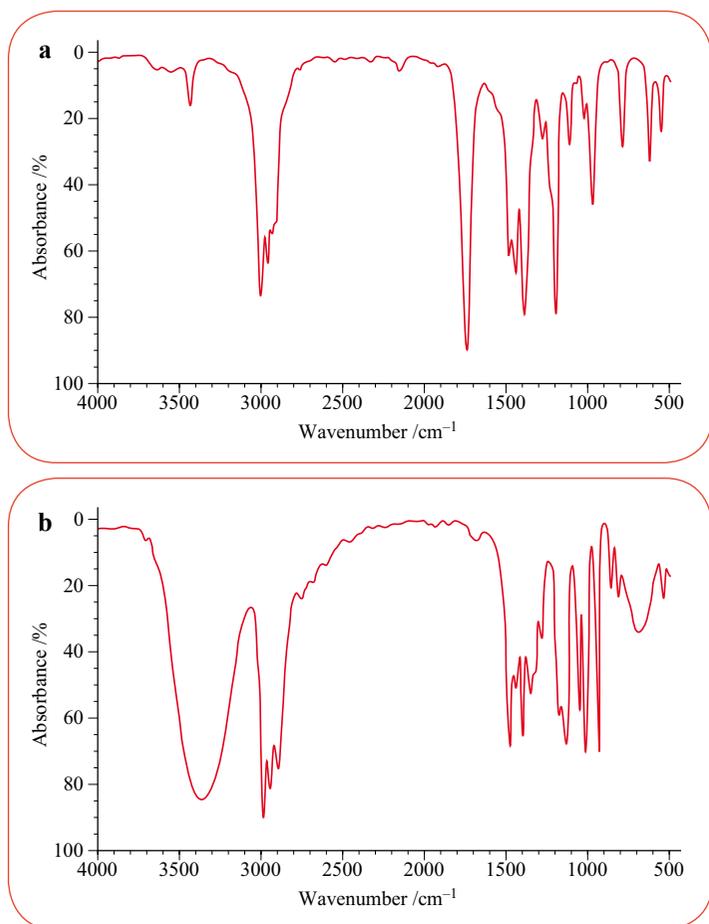


Figure 15.5 The infrared spectra of butanone and butan-2-ol, for use with SAQ 2.

SAQ

- 2 The infrared spectra of butan-2-ol and butanone are shown in Figure 15.5. Identify which of a and b is butanone. Explain your reasoning.

Mass spectrometry

Determination of A_r from mass spectra

You have used relative atomic masses and relative isotopic masses in Chapter 2. You may have wondered how tables of relative atomic masses have been obtained. An instrument called a **mass spectrometer** is used for this purpose; such instruments are too expensive to be found in most schools or colleges. Academic or industrial chemical laboratories may have one or two, depending on their needs and resources. Mass spectrometers have even been sent into space (Figure 15.11).

When a mass spectrometer is used to find the relative atomic mass of an element it does two things. It measures the mass of each different isotope of the element and it measures the relative abundance of each isotope. A vaporised sample of the element is injected into the mass spectrometer. Then the atoms of the element are turned into ions with a positive charge. This is done by electron bombardment. Then the mass spectrometer separates the atoms with different masses, measures the masses of the atoms and counts them.

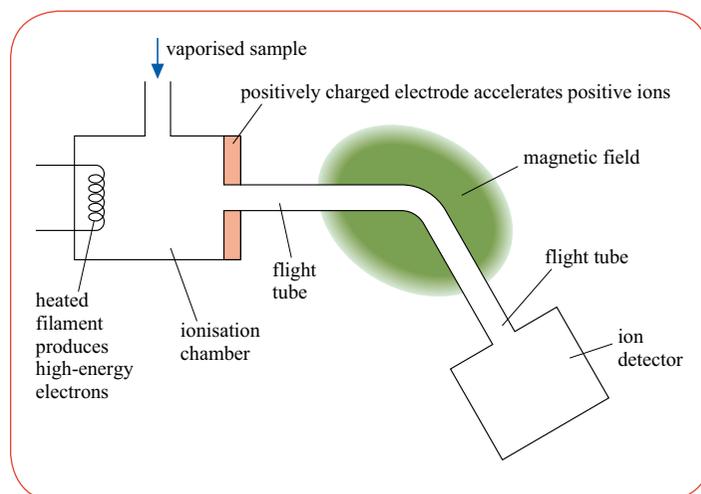


Figure 15.6 Simplified diagram of a mass spectrometer.

A simplified diagram of a mass spectrometer is shown in **Figure 15.6**. (NB You will not be tested on the details of how a mass spectrometer works.)

The results from a mass spectrometer are displayed on a computer monitor as a chart of abundance against mass (see **Figure 15.7** for example, the mass spectrum of germanium). The abundance is on the vertical axis. To be strictly correct the horizontal axis displays the mass-to-charge ratio (m/e), but you will often see this axis simply labelled ‘mass’.

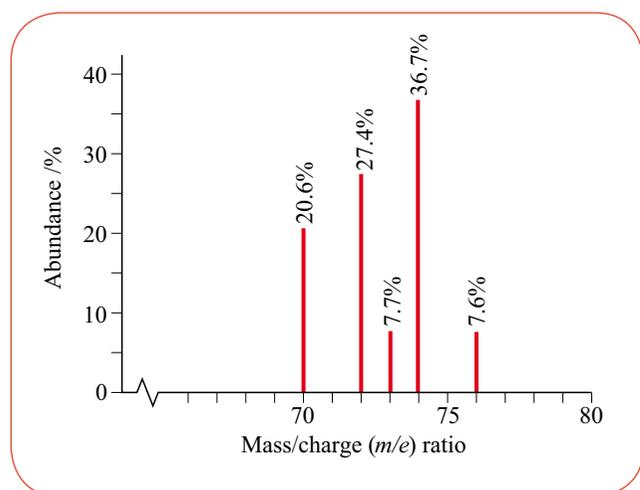


Figure 15.7 The mass spectrum of germanium, Ge.

We can use the data from the mass spectrum to calculate the relative atomic mass, A_r , of germanium. Each peak in the mass spectrum corresponds to a different isotope of germanium. So in the sample we have 20.6% ^{70}Ge , 27.4% ^{72}Ge , 7.7% ^{73}Ge , 36.7% ^{74}Ge and 7.6% ^{76}Ge . Remember that the relative atomic mass takes into account the different proportions of naturally occurring isotopes in an element (see **Chapter 1**). Therefore we have to calculate the weighted mean of the relative masses of the isotopes identified:

A_r of germanium =

$$\frac{(20.6 \times 70) + (27.4 \times 72) + (7.7 \times 73) + (36.7 \times 74) + (7.6 \times 76)}{100} = 72.7$$

Figure 15.9 A high-resolution mass spectrometer. It measures isotopic masses and their abundances very accurately.

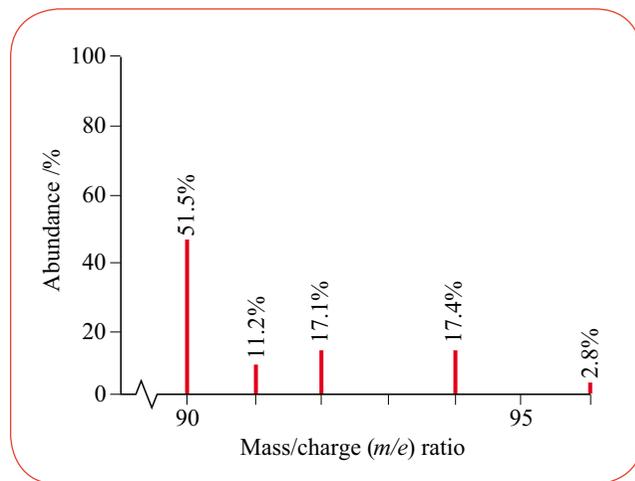


Figure 15.8 The mass spectrum of zirconium, Zr.

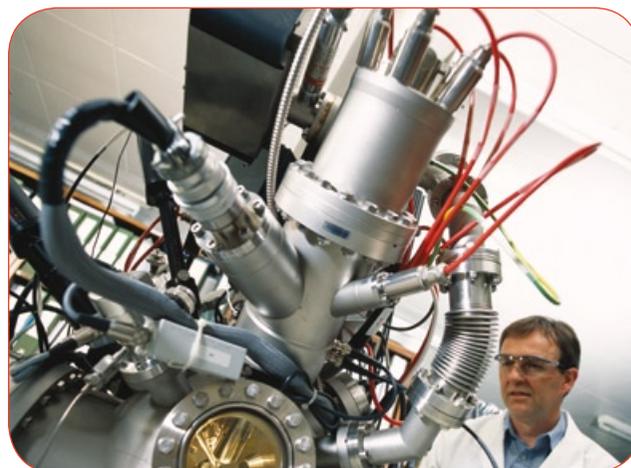
SAQ

- 3 a** Look at the mass spectrum of the element zirconium in **Figure 15.8**. List the isotopes present in zirconium.
- b** Use the percentage abundance of each isotope to calculate the relative atomic mass of zirconium.

Some modern mass spectrometers can be set up to determine isotopic masses to four or five decimal places. **Figure 15.9** below shows a photograph of such a spectrometer.

Using mass spectra to identify unknown substances

The mass spectrometer can also be used to identify unknown organic substances, such as in testing athletes for prohibited drugs. A vaporised sample of the unknown substance is injected into the mass



The Viking space probe



Figure 15.11 The surface of Mars, seen from the *Viking 2* space probe.

When the two *Viking* space probes were launched by NASA in 1975, they carried mass spectrometers. The purpose of these spectrometers was to look for traces of organic compounds on the surface of Mars. Scientists had put forward the hypothesis that living organisms would have left behind traces of organic compounds. However, the soil sampled on Mars showed no trace of organic compounds.

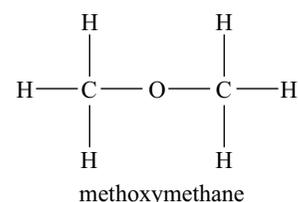
spectrometer. The molecules of the substance are then changed into singly charged positive ions with the same relative molecular mass as the molecules of the unknown compound. These are called the ‘molecular ions’. On the mass spectrum these will appear as the peak at the highest mass. So this peak gives us the relative molecular mass of the unknown compound.

This greatly reduces the number of possible compounds that the unknown could be. However, there will still be alternatives, e.g. if the relative molecular mass is 45, the molecular formula could be C_2H_7N or CH_3NO or any other molecule with this mass.

Organic molecules can also be broken up by the bombarding electrons in the mass spectrometer, to produce positively charged ‘fragments’ of the original molecule. Each fragment has a lower mass than the molecular ion. Look at the mass spectrum of ethanol in [Figure 15.10](#).

SAQ

- 4 A structural isomer of ethanol is methoxymethane. Its structure is shown below.



Predict how the mass spectrum of this compound might differ from ethanol’s mass spectrum shown in [Figure 15.10](#).

Every new compound discovered has its own characteristic mass spectrum which is stored in a computer database. The computer then matches the mass spectrum of the compound to be identified with the correct one from its database. This is called ‘*fingerprinting*’. Infrared spectra are also used for fingerprinting. The fragments formed in a mass spectrometer also can help chemists work out the structure of newly discovered compounds.

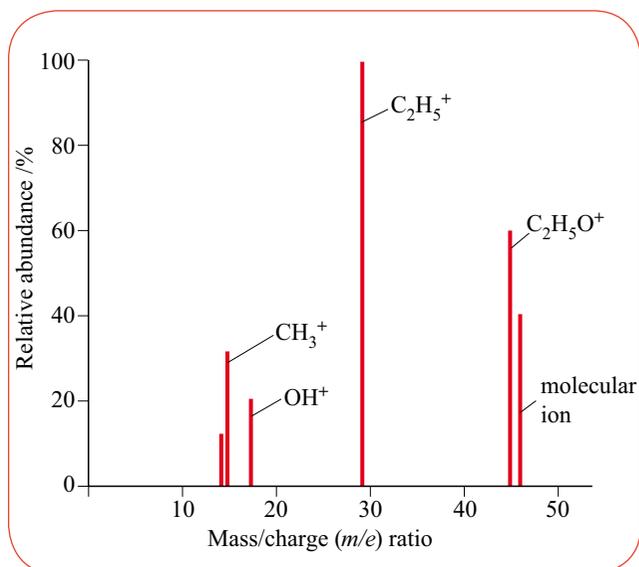


Figure 15.10 The mass spectrum of ethanol, C_2H_5OH . The main fragments have been labelled. Can you see how fragmentation of the ethanol molecule can give rise to each of these ions?

Summary

- Infrared spectrometers analyse the radiation (energy) absorbed by different covalent bonds. This energy causes the bonds to vibrate in a number of different ways, e.g. bending or stretching. Different bonds absorb different parts of the infrared spectrum so they can be identified as being present in a sample.
- Infrared spectroscopy assists in the identification of alcohols, aldehydes and ketones, carboxylic acids and esters by the presence or absence of O–H and C=O absorption frequencies in their spectra.
- Infrared spectroscopy is used to measure the ethanol content of a driver's breath when they are suspected of drink driving.
- Mass spectra of elements enable isotopic abundances to be found and relative atomic masses to be calculated.
- We can also use mass spectroscopy to identify unknown organic compounds by 'fingerprinting' (matching the spectrum to other known spectra). The fragmentation peaks give us clues about the structure of the original molecule.

Questions

Use these characteristic infrared absorptions in organic molecules to help you answer questions 1 to 3.

Bond	Location	Wavenumber /cm ⁻¹
C–O	alcohols, esters	1000–1300
C=O	aldehydes, ketones, carboxylic acids, esters	1680–1750
O–H	hydrogen bonded in carboxylic acids	2500–3300 (broad)
N–H	primary amines	3100–3500
O–H	hydrogen bonded in alcohols, phenols	3230–3550
O–H	free	3580–3670

1 The infrared spectrum of compound **B** is shown below.

Identify:

a the absorption responsible for peak **X**

[1]

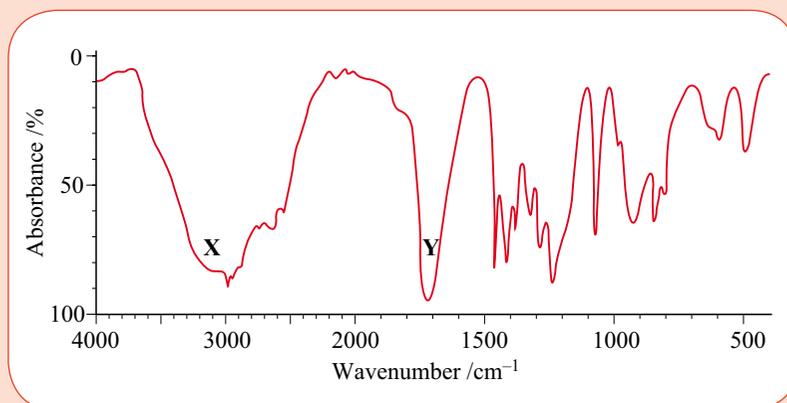
b the absorption responsible for peak **Y**

[1]

c the functional group present in compound **B**.

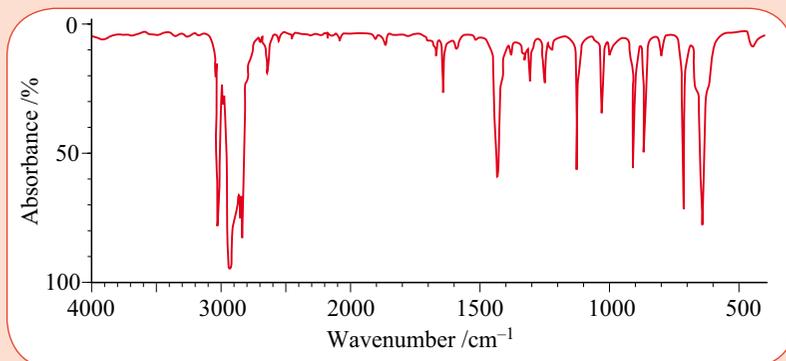
[1]

OCR Chemistry AS (2812) June 2003 [Total 3]



continued

- 2 A student refluxed a solution of chlorocyclohexane and NaOH. The organic product was separated and analysed by infrared spectroscopy. The infrared spectrum of the organic product is shown below.

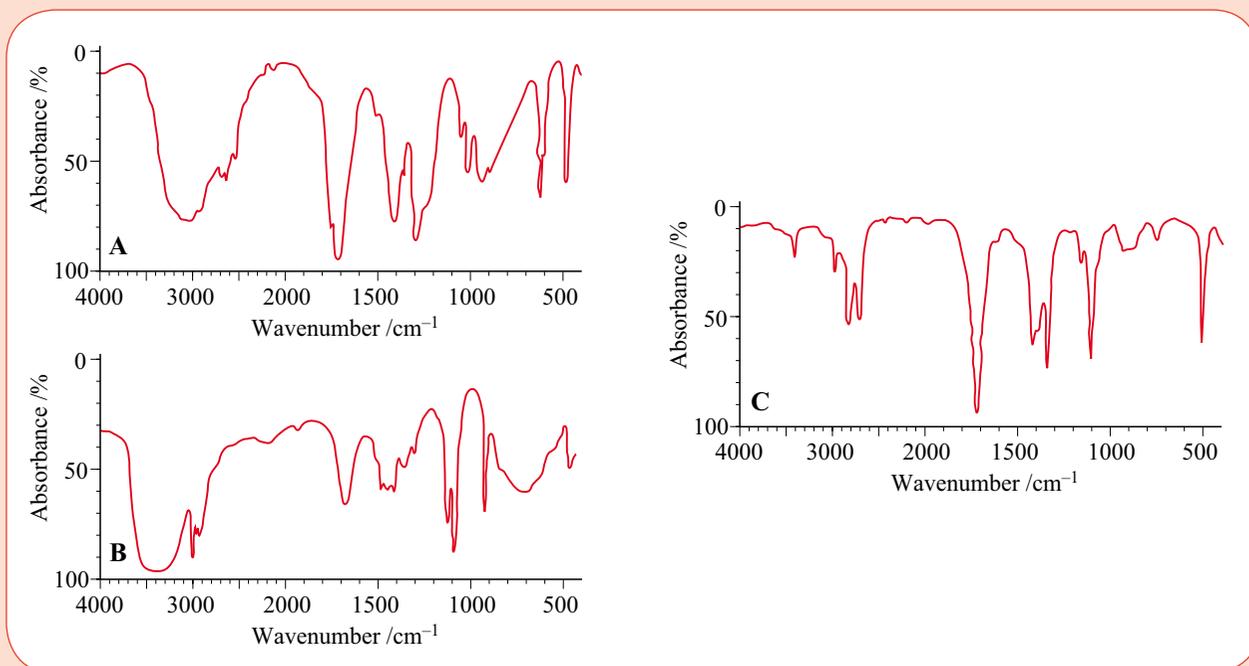


The student used the infrared spectrum to conclude that cyclohexene had been produced. Use the table on [page 177](#) to explain why the student was justified in ruling out cyclohexanol as the organic product.

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[1]
[Total 1]

- 3 Ethanal was analysed by infrared spectroscopy. Use the table on [page 177](#) to justify which of the three spectra shown below is most likely to be that of ethanal. Give three reasons.

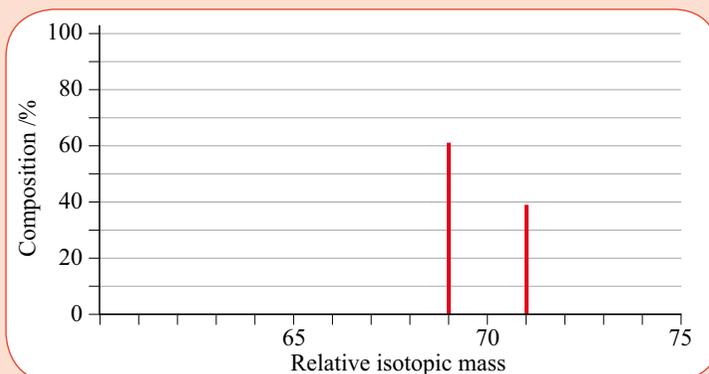


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continued

- 4 A sample of gallium was analysed in a mass spectrometer to produce this mass spectrum. The relative atomic mass of gallium can be calculated from this mass spectrum.



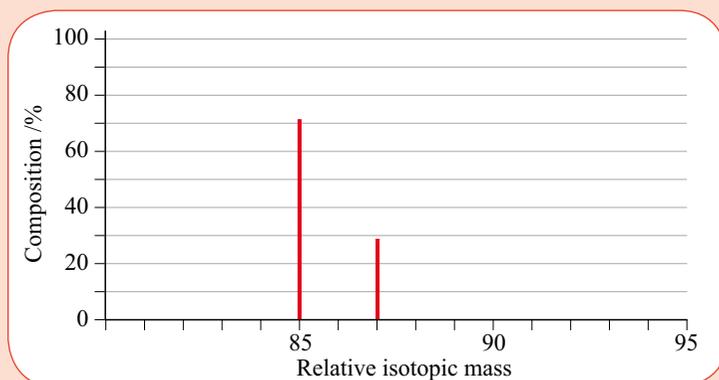
- a Estimate the percentage composition of each isotope present in the sample. [1]
 b Calculate the relative atomic mass of this sample of gallium. Your answer should be given to three significant figures. [2]

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[Total 3]

- 5 Rubidium, atomic number 37, was discovered in 1861 by Bunsen and Kirchoff. Rubidium is in Group 1 of the Periodic Table and the element has two natural isotopes, ^{85}Rb and ^{87}Rb .

- a Explain the term *isotopes*. [1]
 b A sample of rubidium was analysed in a mass spectrometer to produce the mass spectrum below.



- i Use this mass spectrum to help you complete a copy of the table below.

Isotope	Percentage	Number of		
		protons	neutrons	electrons
^{85}Rb				
^{87}Rb				

- ii Calculate the relative atomic mass (A_r) of this rubidium sample. [3]
 Give your answer to three significant figures. [2]
 c Which isotope is used as the standard against which the masses of the two rubidium isotopes are measured? [1]

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[Total 7]