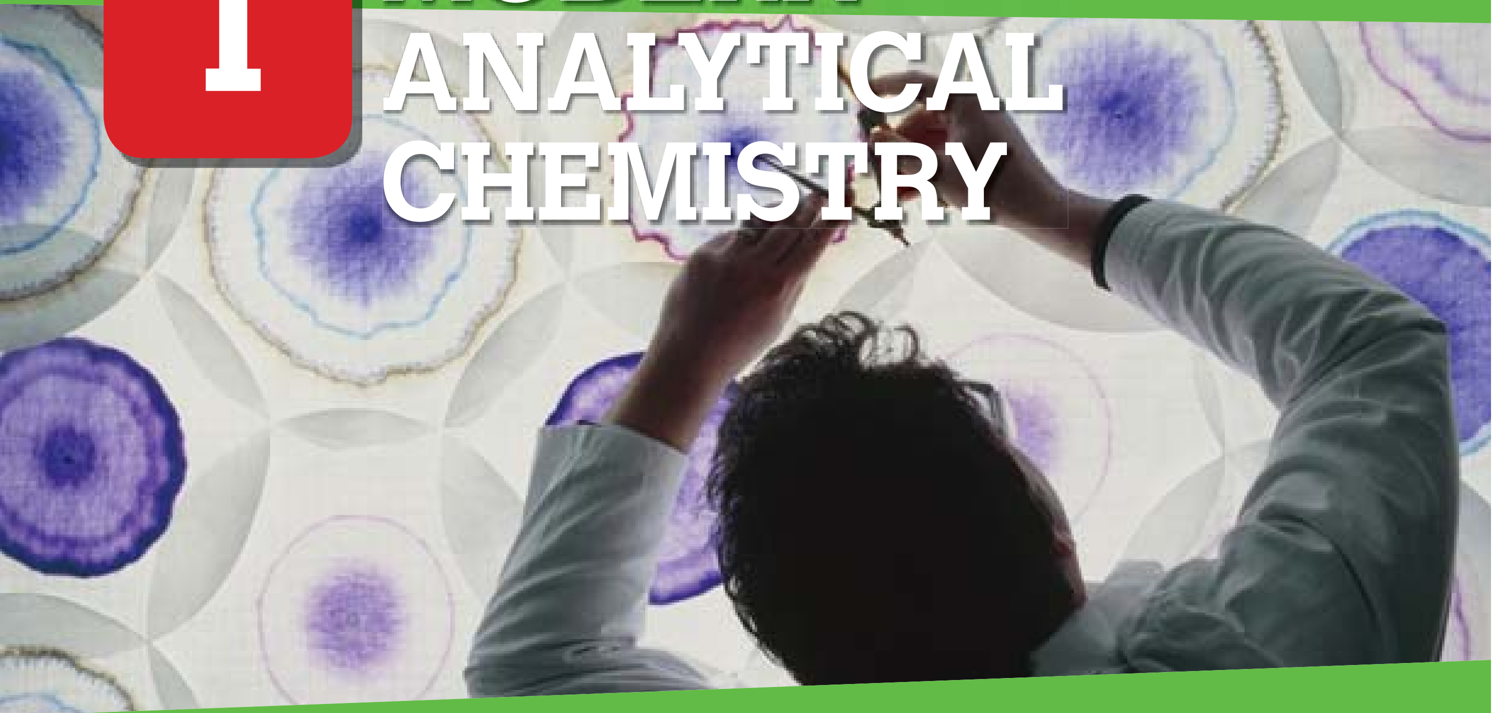
1 MODERN ANALYTICAL CHEMISTRY



Chapter overview

This chapter covers the IB Chemistry syllabus Option A: Modern Analytical Chemistry.

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

- describe the equipment and procedures used for the analysis of substances using atomic absorption (AA) spectrometry, infrared (IR) spectroscopy, mass spectrometry and nuclear magnetic resonance (NMR) spectroscopy
- describe how the structure of compounds may be deduced using information obtained from various spectroscopic techniques
- analyse IR, mass and NMR spectra in order to gain information about molecular structure
- understand that all chromatographic techniques require a stationary phase and a mobile phase
- describe how chromatography is used to identify and quantify the components of a mixture
- use a calibration curve in quantitative chromatographic and spectroscopic analysis
- calculate R_f values and describe the significance of R_f and R_t values in chromatography
- describe the equipment and procedures used for the analysis of substances by paper, thin-layer and column chromatography
- recognize that chromatographic techniques can be used to separate components of a mixture prior to analysis by other techniques such as mass spectrometry and IR spectroscopy

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- describe the equipment and procedures used for the analysis of substances using gas and high performance liquid chromatography
- describe the equipment and procedures used for the analysis of substances using UV–visible spectrometry
- analyse UV–visible spectra in order to gain information about molecular structure
- interpret splitting patterns and chemical shifts in NMR spectra to gain information about molecular structure.

IBO Assessment statements A.1.1 to A.10.2

Figure 1.0.1 A roadside breath test determines whether the blood alcohol content of a driver is over the legal limit.

News reports may tell us that a driver has been arrested for driving with a blood alcohol content of 0.17%, an athlete has been tested for drugs and found to have consumed amphetamines, traces of water vapour have been found in the atmosphere of a new planet and that low fat foods have a high sugar content. How do scientists determine such information? It certainly is not just with the laboratory equipment that we have access to daily. Modern methods of chemical analysis involve the use of instruments that routinely analyse samples rapidly and to high levels of accuracy. Although the instruments may be sophisticated and complex, they all use the basic principles of spectroscopy and chromatography.

1.1 INTRODUCTION TO ANALYTICAL CHEMISTRY

AS A.1.1
State the reasons for using analytical techniques.
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Modern analytical chemistry offers a wide range of problem-solving techniques. Chemists use analytical techniques to identify and confirm the structure of a substance, to analyse its composition and to determine its purity. The quantity and nature of substances present in a mixture may be determined or the progress of a reaction may be followed by analysis. Instrumental analytical techniques are often more accurate and quicker than techniques involving experimental techniques such as those used in acid–base titrations in volumetric analysis or the precipitation of a solid for gravimetric analysis.

Quality control of consumer products requires that the composition of foodstuffs, building materials and even the materials from which our clothes are made be known accurately. Such knowledge can be life saving, or just a guide for people wanting to know the fat content of the food they eat.

Figure 1.1.1 An instrumental analytical technique known as high performance liquid chromatography (HPLC) is used to test the purity of an experimental AIDS vaccine.

In the design and manufacture of drugs, chemical analysis is of the utmost importance. The structure of a newly synthesized compound can be confirmed by spectroscopic methods and its purity measured by chromatographic methods.

Although there may be many analytical instruments with varied components, they are essentially of only three types: those based on the interaction of electromagnetic radiation with the sample (spectroscopic techniques), those based on the interaction of magnetic and/or electric fields with the sample (mass spectroscopy and nuclear magnetic resonance) and those involving chromatography. Instrumental methods have several advantages over the more traditional laboratory methods (volumetric and gravimetric). They are faster, more sensitive, more accurate and less prone to human error. Their main disadvantage is cost!

Analytical techniques

In an attempt to prevent cheating in sport, the urine of competitors is regularly tested for the presence of performance-enhancing drugs. In many schools, students suspected of illicit drug use may also find themselves requested to undergo such tests. Chromatography is the basis of the drug-testing cards that are used in these situations. In such 'dipstick' tests, a simple colour change in the chemically treated panel of the card indicates the presence of the drug for which the urine is being analysed.

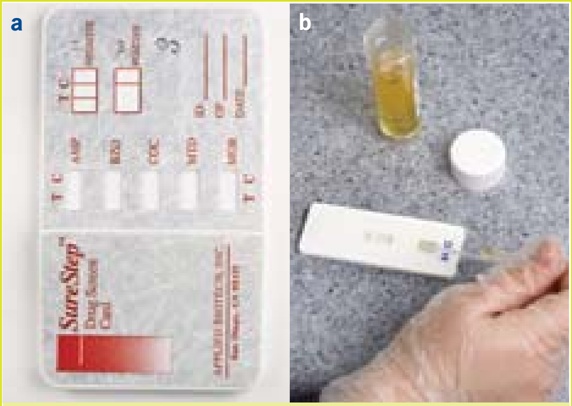


Figure 1.1.2 (a) A drug test card is a simple way to test for the presence of drugs in urine. (b) A pregnancy can be confirmed by a simple urine test for the presence of a particular hormone (hCG).

Chemical analysis is widely used in medicine for the detection of unwanted substances in the blood or urine. For example, the initial test for diabetes involves measuring the amount of glucose in the blood and ketones in the urine. Home pregnancy kits are another example of a urine 'dipstick' test. These kits contain a treated panel that will change colour in the presence of a hormone called human chorionic gonadotrophin (hCG).

Although chemical dipsticks are used for identification of a substance in the urine or blood, the exact amount is often determined by instrumental methods. The concentration and identity of a compound in blood or urine can be determined using chromatography (in particular gas–liquid chromatography) and spectroscopy.

Modern chemical analysis can detect the presence of tiny, yet toxic, quantities of elements in our water supply and in our air. The technique of atomic absorption spectroscopy can detect up to 70 different metal elements in concentrations as low as parts per billion (ppb = μg per kg) of sample. Environmental protection authorities can use this method to analyse samples of water or air for pollution.

Forensic science makes extensive use of modern chemical analytical methods. The presence of toxic chemicals in tissue samples or hair can be determined using high performance liquid chromatography. This may well reveal the cause of death of a murder victim.

Spectroscopy and chromatography both provide the opportunity for samples to be analysed qualitatively and quantitatively. In **qualitative analysis**, the *identity* of a sample, or its components is determined, whereas **quantitative analysis** is used to determine the *amount* of the sample or its components. The outputs from spectroscopic and chromatographic instruments have several common features. Spectra and chromatograms both show a series of peaks that can be used both qualitatively and quantitatively. The position of a peak on the horizontal axis provides information that identifies the substance causing the peak, while the peak area provides information that can be used to determine the amount of that substance.

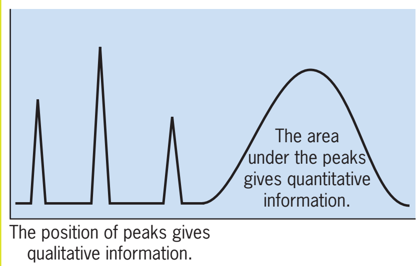


Figure 1.1.3 Spectra and chromatograms have several features in common.

Faced with this array of instrumental techniques, how does a chemist choose the most appropriate technique for analysing a particular sample? Such decisions will depend on a number of factors:

- Is qualitative or quantitative information required?
- How much material is available for analysis?
- How low is the concentration of the component being analysed likely to be?
- What is the chemical nature of the sample?
- What is the level of expertise of the chemist?
- What accuracy is required?

and, of course, the ever practical question:

- How much money is available for the analysis?

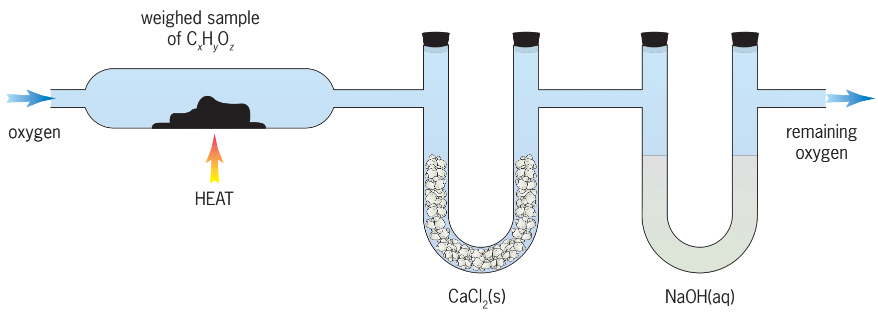


Figure 1.1.4 Determining the empirical formula of an unknown compound.

CHEM COMPLEMENT

Chemical analysis—the natural way

While many analytical instruments are able to accurately detect and measure minute quantities of substances, few come close to the sensitivity shown by natural systems. Organisms have built-in detection devices that form part of the complex control systems used to regulate the levels of critical chemicals such as hormones and neurotransmitters. Chemists are now making use of these supersensitive biodetectors. For example, hairs from Hawaiian red swimmer crabs can be attached to electrical analysis equipment to detect hormones at concentrations as low as 10^{-12} mol dm^{-3}!

AS **A.1.2 State that the structure of a compound can be determined by using information from a variety of analytical techniques singularly or in combination. © IBO 2007**

Consider, for example, the analysis of an unknown organic compound to determine its molecular and structural formula. Classically, a sample of the compound would be burnt in air to produce water, carbon dioxide and any other products. From measurements of the masses of the compound and the products, an empirical formula could be determined. Molar mass, and hence molecular formula, could be determined using measurements of gaseous samples. Finally, chemical tests for functional groups would be conducted. Much of this 'classic' chemistry has been replaced by modern instrumental methods. When such chemical methods are used in conjunction with instrumental methods, chemists can quickly and accurately determine the structural formula of a compound.

A mixture of hydrocarbons may first be separated into its components by high performance liquid chromatography. Then each component can be passed through a mass spectrometer to find its molecular mass and to determine its likely structure. This information may be supported by infrared spectroscopy, which is used to determine the nature of any functional groups. Information from only one technique is usually insufficient to determine or confirm a structure; the results from many different instrumental techniques are used in combination. One major advantage of using instrumental techniques is that great detail can be obtained from a very small amount of substance.

Principles of spectroscopy

AS **A.2.1 Describe the electromagnetic spectrum © IBO 2007**

The basis of spectroscopic analysis is the effect of electromagnetic radiation on matter. The sample for analysis is exposed to electromagnetic radiation and the effects of the interaction monitored. The study of the radiation absorbed or emitted by matter is called **spectroscopy**. The measurement of the amounts of light absorbed or emitted is called **spectrometry**. Instruments used for viewing the results of interactions between the sample and the radiation are called **spectrometers**. More elaborate instruments that measure amounts of radiation are called **spectrophotometers**. A wide variety of spectroscopic instruments are used in industry. Such instruments include atomic absorption and UV–visible spectrophotometers, and infrared spectrometers.

To understand spectroscopy, we need to review our basic understanding of the electromagnetic spectrum. Light consists of electromagnetic waves. The **wavelength** (distance between successive crests) of visible light ranges from about 8×10^{-7} metres for red light to about 4×10^{-7} metres for violet light. The **frequency** (the number of waves passing a given point each second) of light ranges from about 4×10^{14} for red light to about 7×10^{14} for violet light.

The wavelength and energy of light are related by the equation:

$$E = h\nu = \frac{hc}{\lambda}$$

where ν is the frequency
E is the energy
λ is the wavelength
c is the speed of light (3×10^8 m s^{-1})
h is a constant
(Planck's constant = 6.63×10^{-34} J s)

The energy of light increases as the wavelength decreases, showing an inverse relationship.

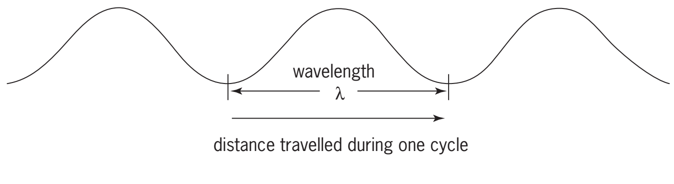


Figure 1.1.5 The wavelength of an electromagnetic wave is the distance travelled by the wave during one cycle. Its frequency is the number of waves that pass a particular point every second.

Of all the colours of visible light, violet light has the highest energy (and shortest wavelength) while red light has the lowest energy (and longest wavelength). Light is part of the broader electromagnetic spectrum, which also includes gamma rays, X-rays, ultraviolet (UV) rays, infrared (IR) waves, microwaves and radio waves.

Wavenumber is another wave property, and is equal to the inverse of wavelength ($\frac{1}{\lambda}$). Wavenumber corresponds to the number of cycles the wave produces in a centimetre and has the units cm^{-1}. The wavenumber has traditionally been the most common method of specifying IR absorption (see section 1.2).

Interactive Animation
Electromagnetic spectrum

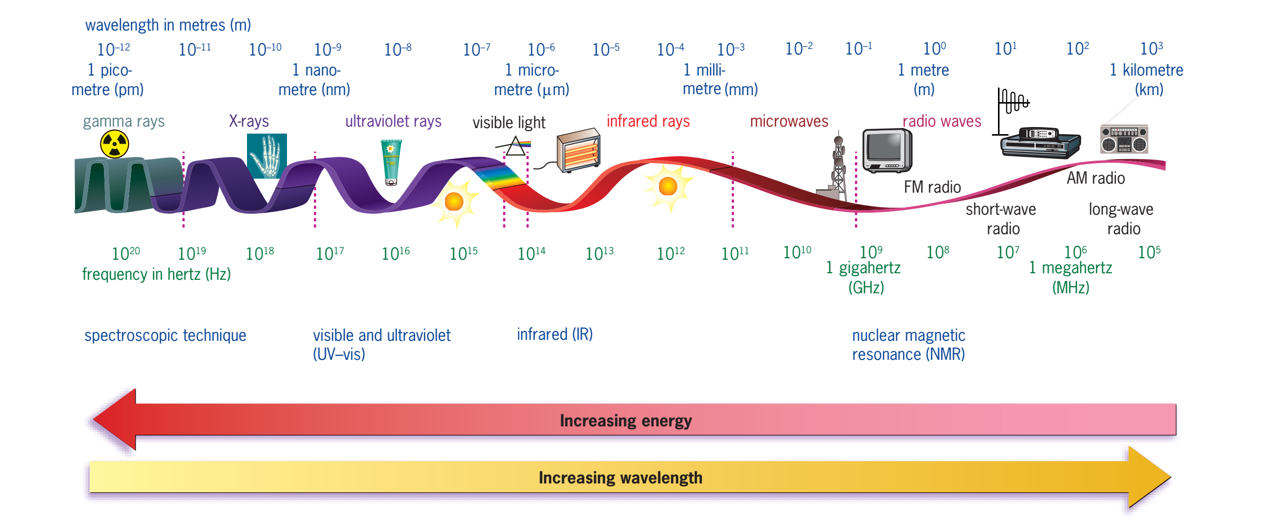


Figure 1.1.6 The electromagnetic spectrum. Different spectroscopic techniques use radiation from different parts of the spectrum.

When sunlight (which contains all wavelengths of visible light) passes through a prism, the different wavelengths are bent (or refracted) through different angles so that the light is broken into its components, producing a continuous spectrum of colours.

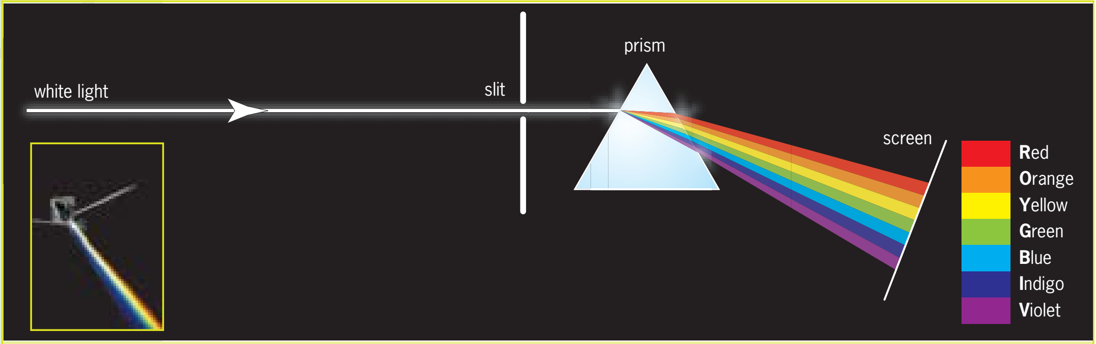


Figure 1.1.7 White light produces a continuous spectrum (ROYGBIV) when passed through a prism.

AS A.2.2 Distinguish between *absorption* and *emission* spectra and how each is produced.© IBO 2007

In chapter 4 of *Chemistry: For use with the IB Diploma Programme Standard Level*, we discussed atomic emission spectra (line spectra). These occur when energy is given to an atom, in the form of heat, electricity or light. An electron can move between energy levels within the atom if it absorbs energy that corresponds to the difference between two energy levels. When an electron moves to a higher energy level, the atom is said to be in an **excited state**. Electrons in higher than usual energy levels are unstable. They quickly return to their lower energy level, their **ground state**, by emitting the energy previously absorbed. This energy is released in the form of light.

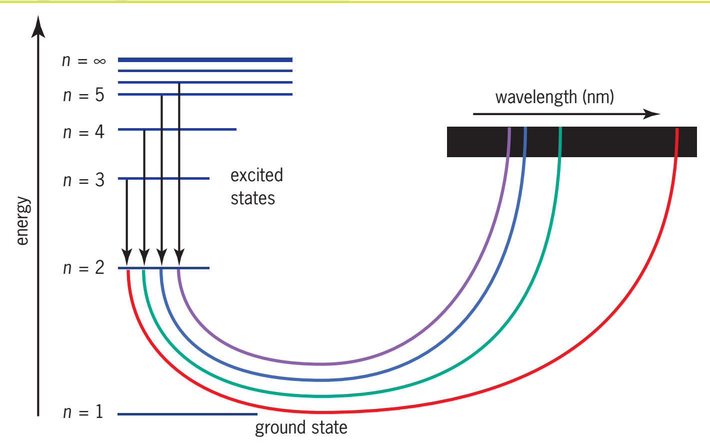


Figure 1.1.8 When electrons move from higher to lower energy levels, they emit light energy.

The energy of the emitted light is equal to the difference in energy between the higher and lower energy levels. Transitions between different energy levels release light of differing wavelengths according to the relationship $E = \frac{hc}{\lambda}$. As several electron transitions are possible, several colours of light could be emitted (although only the most intense colours might be detected by the unaided eye).

Atoms of different elements have different numbers of protons and therefore electrons. They also have different energy levels. Each type of atom will therefore emit light that has a unique set of energy values. This is the basis for **atomic emission spectroscopy**. In atomic emission spectroscopy a very hot flame is used to excite a wide range of metals and the emitted light is passed through a prism, producing an emission spectrum. Light emitted from excited atoms contains only certain characteristic wavelengths of light, which have been produced by the transition of electrons from one energy level to another. When this light is passed through a prism, the spectrum produced is a series of coloured lines separated by 'black' gaps. Such a spectrum is called an **emission** or **line spectrum**. Each metal atom produces a unique line spectrum that can be compared with the line spectrum produced by an unknown sample. If the lines match in terms of intensity, position and frequency of occurrence, it can be established that the unknown sample contains a specific metal(s).

PRAC 1.1
Flame tests and emission spectra

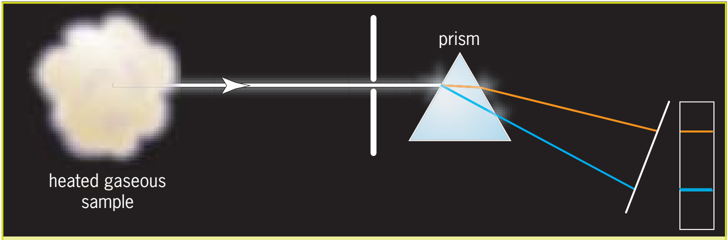


Figure 1.1.9 Light emitted from excited atoms produces an emission spectrum when passed through a prism.

Interactive Animation
Emission spectroscopy

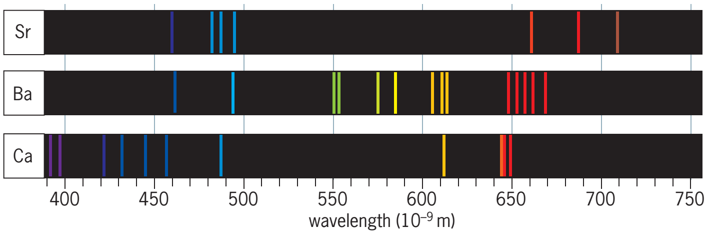


Figure 1.1.10 Emission spectra for a number of elements.

QuickTime Video
Flame tests for metals

If the energy supplied to a cool gaseous element is light, rather than heat, the element can absorb exactly the frequencies of light that are required to excite electrons to higher energy levels. When the remaining light is passed through a prism, 'gaps', black lines on the otherwise continuous spectrum can be seen. This pattern of black lines on the coloured background is an **absorption spectrum**. The black lines on the background of the continuous spectrum represent those energies of light absorbed by electrons moving from the ground state to higher energy levels. This spectrum is also a *line spectrum*. The absorption spectrum will be the complement of the emission spectrum (since the same amounts of energy are involved when electrons absorb and then emit light).

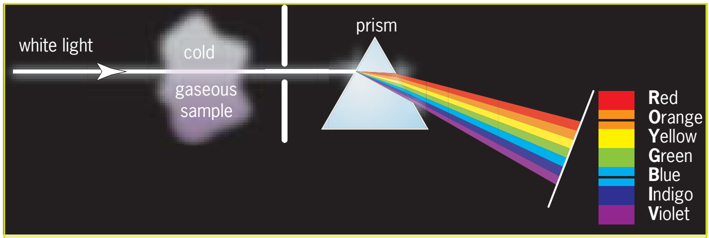


Figure 1.1.11 Light absorbed by atoms produces an absorption spectrum when passed through a prism.

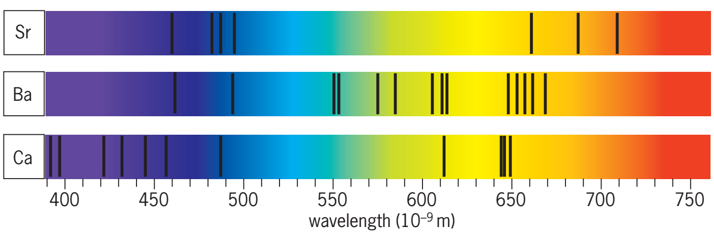


Figure 1.1.12 Absorption spectra for a number of elements.

A.2.3
Describe the atomic and molecular processes in which absorption of energy takes place. © IBO 2007

As we have seen in the example of absorption spectroscopy, electromagnetic radiation interacts with atoms and molecules. The nature of this interaction depends upon the energy (and hence the wavelength) of the electromagnetic radiation. In the case of absorption spectra, the absorption of energy from visible light by atoms results in electrons being excited and moving to higher energy electron shells. When molecules are involved, electronic transitions are not always the only possibility. As the electromagnetic radiation being absorbed decreases in energy (ultraviolet/visible → infrared → radio waves), the way in which it affects the molecule changes.

If the energy is in the ultraviolet or visible region of the electromagnetic spectrum, enough energy is available for absorption that results in electrons moving up to higher energy levels (electron transition). The spectroscopic technique that makes use of this is called **UV–visible spectroscopy** (see section 1.6). If the electromagnetic radiation is in the infrared region, it is not of sufficiently high energy to move the electrons to higher energy levels. Instead the atoms in a molecule may be made to vibrate in a characteristic manner. The absorption of this electromagnetic radiation results in transitions in vibrational states. These absorptions are not perfectly sharp, they are, in fact, absorption 'bands'. High resolution infrared spectrometers show that for molecules such as HCl, the bands are actually made up of a series of closely spaced absorptions. This occurs because changes in rotation (rotational transitions) often accompany vibrational transitions. This analytical technique is called **infrared spectroscopy** (see section 1.2). At even lower energies, at the frequency of radio waves, the absorption of energy relates to transitions between nuclear-spin energy levels. This is **nuclear magnetic resonance (NMR) spectroscopy** (see section 1.3).

CHEM COMPLEMENT

Investigating space using spectra

Collecting samples of extraterrestrial material is difficult. While material from the Moon and Mars has been analysed directly, most of the information we have about materials in space comes from the light they emit or absorb. In 1802 William Wollaston, an English chemist, noted a number of dark lines in the continuous spectrum of sunlight. These lines were independently rediscovered in 1817 by the German physicist Joseph von Fraunhofer, who studied the lines systematically and measured the wavelengths at which they occurred. He later discovered dark lines in the spectra of stars and noted that some of the lines in these spectra were absent from the Sun's spectrum and vice versa. This clearly indicated that not all of the lines came from the Earth's atmosphere. This led to the proposition that these lines were caused by absorption of the light by elements in the upper layers of the Sun as it passed out towards the Earth. These lines were named Fraunhofer lines in recognition of the careful work done by Joseph von Fraunhofer.

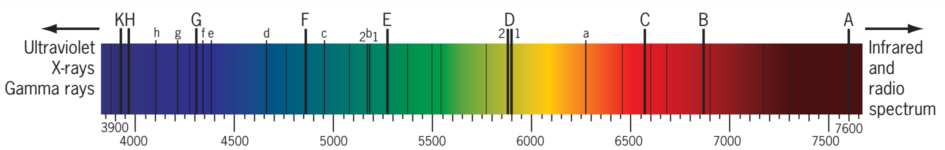


Figure 1.1.13 Fraunhofer lines represent the absorption of light from the Sun by elements in the Sun's outer layers.

Section 1.1 Exercises

1 Describe three general applications of analytical techniques.

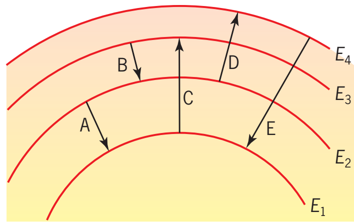
2 Describe how wavelength changes across the electromagnetic spectrum, giving specific examples of regions with long and short wavelengths.

3 Distinguish between wavelength and wavenumber.

4 Which one of the different colours of light in the visible light region of the electromagnetic spectrum has the highest energy? Explain your choice.

5 Explain the basis of all forms of spectroscopic analysis.

6 A representation of the energy levels of an atom is shown. Shown on the diagram are a number of electron transitions, labelled A to E.



- **a** State which transitions would produce lines on an emission spectrum.
- **b** State which transition produce radiation with the longest wavelength.
- **c** Identify the transition that would emit or absorb the largest amount of energy.
- **d** Identify the transitions that involve the absorption of energy.

7 Compare the emission and absorption spectra of hydrogen.

8 Describe what happens to the molecules of a compound when they absorb infrared light.

1.2 INFRARED SPECTROSCOPY

AS A.3.3 Explain what occurs at a molecular level during the absorption of IR radiation by molecules. © IBO 2007

Infrared spectroscopy is a very useful form of spectroscopy, especially in the identification of organic compounds. The infrared region of the electromagnetic spectrum is not of high enough energy to excite electrons to higher states. However, molecules can absorb infrared radiation and changes occur to their bonds. Molecules are not rigid structures; their covalent bonds can be compared to springs that can be stretched or bent. The atoms within a molecule continually move, resulting in the vibrational and rotational motion of the molecule. Vibrations of the molecule equate to the atoms in the molecule changing position as their bonds bend or stretch. You will recall that electrons can only occupy discrete electronic energy levels (shells). Similarly, molecules are only able to occupy discrete vibrational energy levels. Absorption of infrared radiation will give a molecule enough energy to move from one vibrational energy level to a higher (excited) vibrational energy level.

Interactive Animation: Molecular vibrations

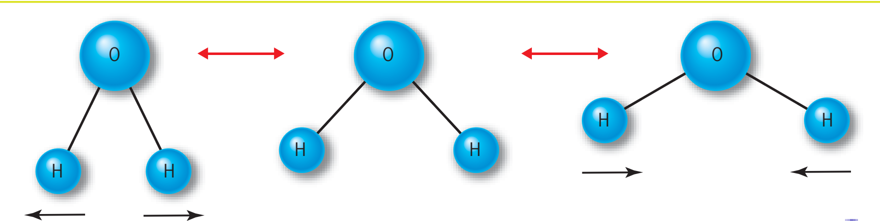


Figure 1.2.1 As a water molecule vibrates, the H—O—H bond angle changes.

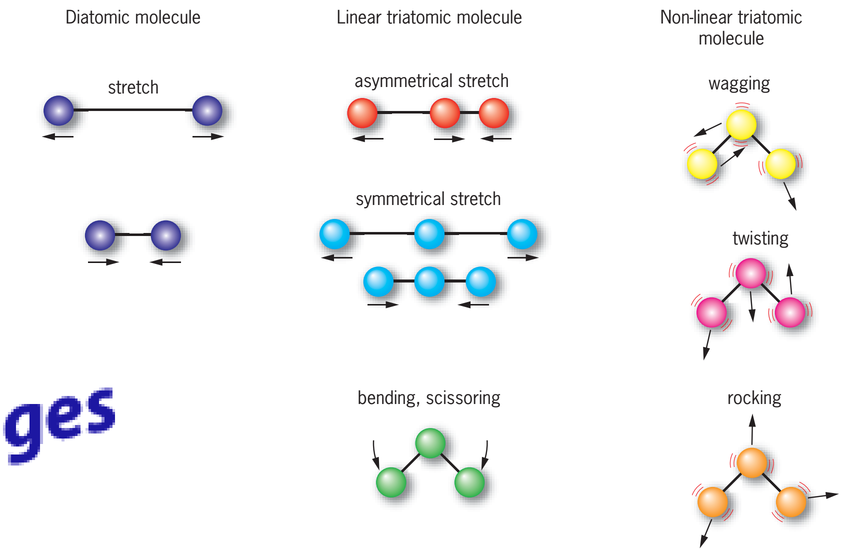


Figure 1.2.2 Diatomic and triatomic molecules can undergo a range of different stretching and bending motions.

When a molecule absorbs infrared radiation, the bending or stretching vibrations change the polarity of the bond and hence the overall dipole moment of the molecule. The dipole moment is a measure of the strength and direction of the charge separation in a molecule. It depends on both the polarities of the individual bonds and the geometry of the molecule. Consider the water molecule in figure 1.2.1. As the hydrogen atoms bend away from each other, the geometry of the molecule changes, so its dipole moment changes. Sulfur dioxide, SO_2, would show a similar change in dipole moment as the molecule bends. Carbon dioxide, a linear triatomic molecule (see figure 1.2.2) could undergo symmetrical and asymmetrical stretching, as well as bending, which would also change its overall dipole moment from zero to a non-zero value. A $-CH_2-$ group in a hydrocarbon would change its geometry as it undergoes stretches similar to those of the non-linear triatomic molecule in figure 1.2.2. A small number of molecules, such as O_2 and N_2, do not absorb IR radiation because they are diatomic molecules made up of identical atoms. Neither the covalent bond, nor the molecule overall has a dipole moment.

Double-beam spectrometry

AS A.3.1
Describe the operating principles of a double-beam IR spectrometer. © IBO 2007

The main features of a double-beam infrared spectrometer are:

- a source of infrared radiation
- a wavelength selector (**monochromator**)
- a beam splitter, which creates two beams that follow parallel paths
- a sample cell and a reference cell or disc made out of solid NaCl or KBr. (Glass and plastic cannot be used, as they absorb IR radiation, so are opaque to IR radiation.)

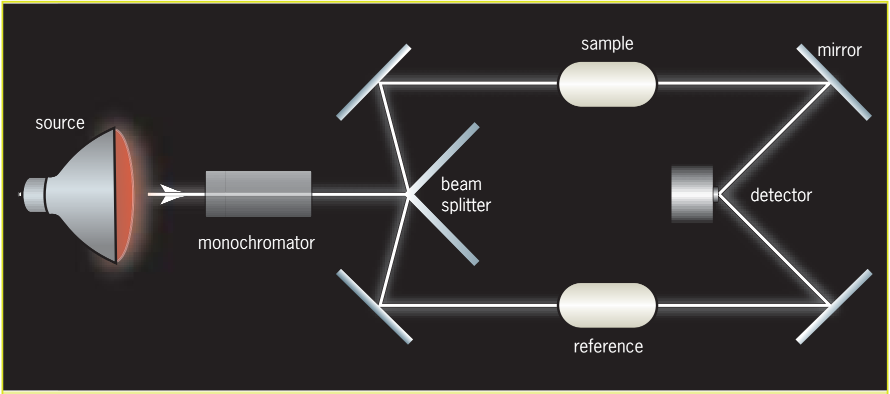


Figure 1.2.3 The double-beam IR spectrometer.

A double-beam infrared spectrometer (or spectrophotometer) allows the radiation passing through the sample to be continually compared with identical radiation that has not passed through the sample. Radiation from the source passes through a monochromator, which only allows radiation of a particular wavelength to pass through. This radiation then strikes a beam splitter and is split into two beams that pass along parallel paths. One beam passes through the cell containing the sample, the other passes through an identical reference cell that contains the same solvent etc. but no sample. The two beams are recombined at the detector. The signals from the sample and reference beams are compared electronically to determine the amount of absorbance due to the sample.

Analysing an IR spectrum

Organic molecules are usually made of several different atoms joined by a variety of covalent bonds. The absorbance of infrared radiation affects these bonds differently. In particular, infrared spectroscopy is important for the information we can obtain about the **functional groups** in the molecule. These groups differ in their composition (the atoms involved in the group) and in the strength of the bonds between the atoms (double or triple bonds). Generally, the range of energies absorbed depends on the strength of the bonds. The stronger the bond (higher bond enthalpy), the higher the value of energy that it absorbs.

AS A.3.2
Describe how information from an IR spectrum can be used to identify bonds.
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TABLE 1.2.1 BOND STRENGTH (BOND ENTHALPY) AND ENERGY NEEDED TO EXCITE A MOLECULE TO A HIGHER VIBRATIONAL ENERGY LEVEL

Bond	Average bond enthalpy (kJ mol^{-1})	Infrared absorption range due to stretching vibrations (cm^{-1})
C=C	612	1610–1680
C≡C	837	2100–2260
C–O	360	1050–1410
C=O	743	1700–1750

The mass of the atoms attached by the bond also affects the energy of the infrared radiation absorbed. The higher the mass, the lower the value of the energy of the radiation absorbed. This can be seen in the absorbance of the halogenoalkanes.

TABLE 1.2.2 THE EFFECT OF CHANGING THE MASS OF THE HALOGEN ON THE INFRARED ABSORPTION

Bond	Infrared absorption range due to stretching vibrations (cm^{-1})
C–I	490–620
C–Br	500–600
C–Cl	600–800
C–F	1000–1400

Functional groups in different molecules absorb IR radiation at slightly different values, so an absorption range, rather than a particular value, is assigned to each functional group. The position of an infrared band in an IR spectrum is defined by a wavenumber (cm^{-1}). Radiation with a short wavelength will have a high wavenumber, since a large number of cycles will fit into a centimetre. Conversely, as wavenumber is the reciprocal of wavelength, radiation with a high wavenumber will have a short wavelength. The intensity of a peak on an IR spectrum is measured as % transmittance. A low value of % transmittance indicates that there has been strong absorption of the radiation with that wavenumber.

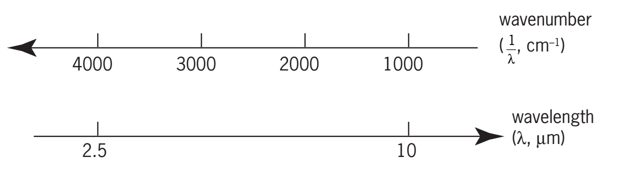


Figure 1.2.4 Wavenumber is the reciprocal of wavelength, so radiation with a high wavenumber has a short wavelength.

AS A.3.4 Analyse IR spectra of organic compounds. © IBO 2007

The result of passing infrared radiation through an organic compound is an infrared spectrum (see figure 1.2.5) showing the % transmittance (or simply transmittance) at different wavenumbers.

As illustrated in figure 1.2.5, each trough (upside-down peak) is called a *band*. Recall that the strength of the covalent bond will determine the energy of radiation absorbed. Each type of bond absorbs infrared radiation over a typical narrow range of wavenumbers. Like a spring, the bond is stretched by the absorption of energy. For example, radiation of higher energy (and hence higher wavenumber) is needed to stretch an O–H bond in an alcohol than a C–H bond, and much less energy is needed to stretch a C–O bond in the same alcohol (see figure 1.2.6).

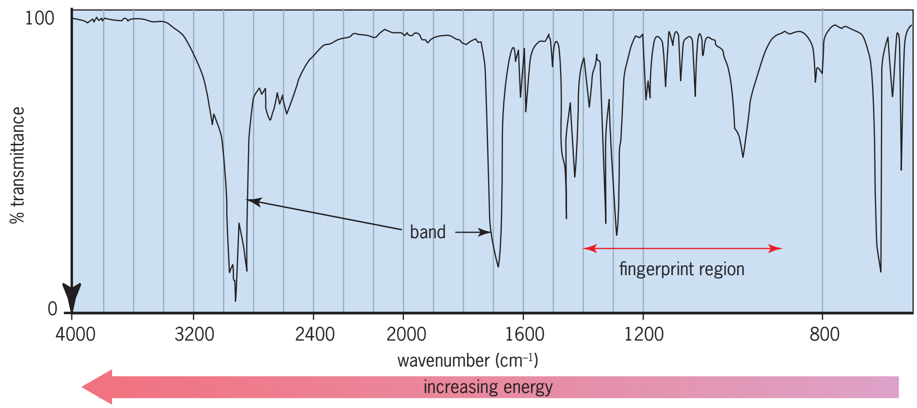


Figure 1.2.5 An infrared spectrum shows a complex series of bands.

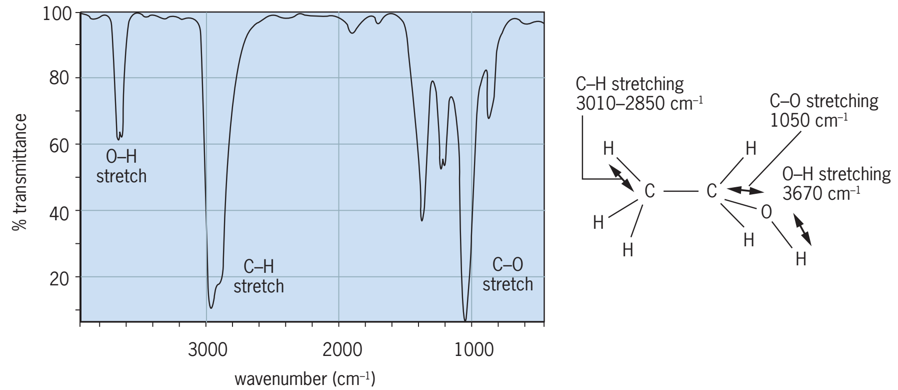


Figure 1.2.6 The infrared spectrum of ethanol shows bands corresponding to the stretching of O–H, C–H and C–O bonds.

Because the functional groups in the organic compound being analysed absorb at characteristic wavenumbers, these characteristic spectral bands can be used to identify specific functional groups within a molecule. Table 1.2.3 shows some of the common functional groups and their characteristic wavenumbers. Some bands, such as the C=O (carbonyl) band, are very useful because they are specific to a limited number of compounds (carboxylic acids, ketones, aldehydes and esters). Others, such as the C–H band, are of limited use because there are so many of them in all organic compounds.

TABLE 1.2.3 CHARACTERISTIC RANGES FOR INFRARED ABSORPTION DUE TO STRETCHING VIBRATIONS OF VARIOUS FUNCTIONAL GROUPS

(These values can also be found in table 17 of the IB Data Booklet. © IBO 2007)

Functional group	Organic molecules in which it is found	Wavenumber (cm^{-1})
C–I	Iodoalkanes	490–620
C–Br	Bromoalkanes	500–600
C–Cl	Chloroalkanes	600–800
C–F	Fluoroalkanes	1000–1400
C–O	Alcohols, esters, ethers	1050–1410
C=C	Alkenes	1610–1680
C=O	Aldehydes, ketones, carboxylic acids, esters	1700–1750
C≡C	Alkynes	2100–2260
O–H	Carboxylic acids	2500–3300
C–H	Alkanes, alkenes, arenes	2850–3100
O–H	Alcohols, phenols	3200–3600
N–H	Primary amines	3300–3500

Interpreting an infrared spectrum requires considerable skill and practice. Bands may overlap, and various neighbouring groups in the molecule may shift the absorption bands of a particular group. Figure 1.2.7 shows the infrared spectrum for 2-methylpropanoic acid, with the characteristic absorption peaks labelled.

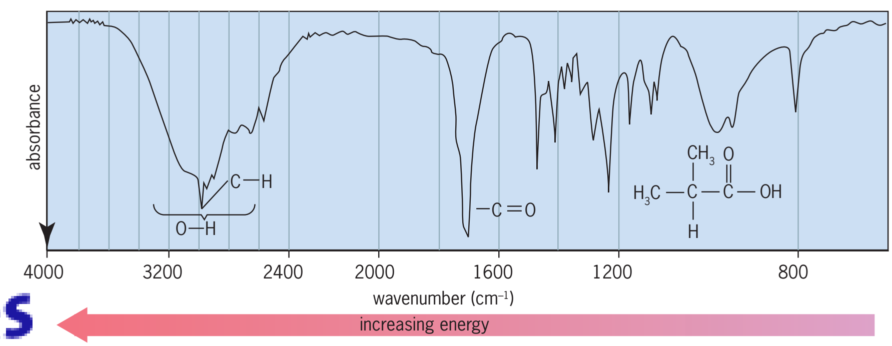


Figure 1.2.7 Infrared spectrum of 2-methylpropanoic acid ($CH_3CH(CH_3)COOH$).

Note that functional group isomers may have very similar infrared spectra. In such cases it may only be possible to identify the bonds present in a molecule, rather than the functional groups.

These difficulties aside, we can look at infrared spectra and recognize some of the more striking bands, and correlate the information with that provided by other types of spectral data. An experienced interpreter would, of course, be expected to gain far more information.

In addition to providing information about functional groups, the infrared spectrum of a molecule can be used as its 'fingerprint'. The region between 900 cm^{-1} and 1400 cm^{-1} of the absorption spectrum is complex and is known as the *fingerprint region*. If this region of the spectrum of an unknown compound is the same as that of a known compound, an identification can be made. Note that the two spectra in figure 1.2.8 have quite different fingerprint regions, even though they both show absorption peaks that correspond to the stretching of C–H bonds and C=O bonds.

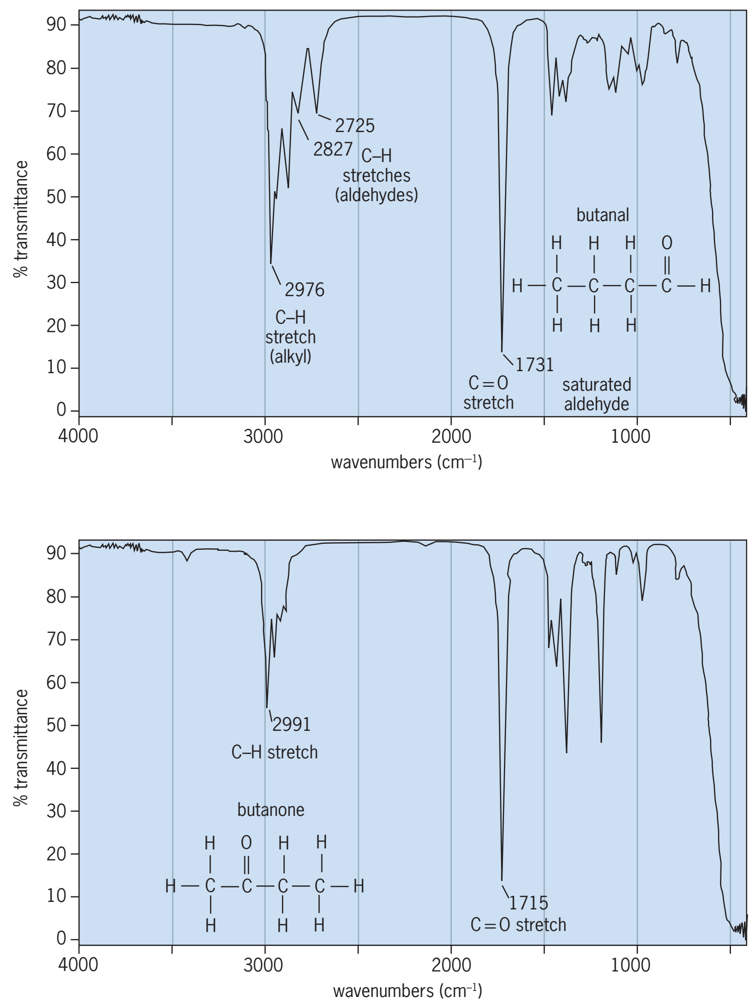


Figure 1.2.8 The infrared spectra of butanal and butanone are very similar.

Worked example 1

The structural formula and infrared spectrum of ethanol is shown in figure 1.2.9. Use table 1.2.3 to identify the bond types corresponding to peaks A, B and C

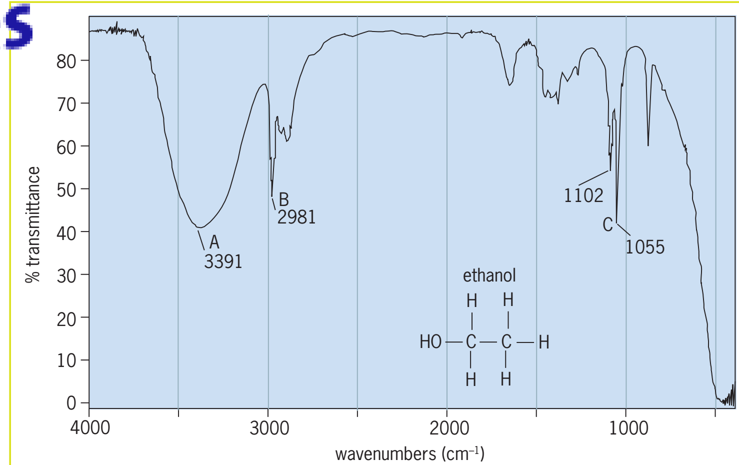


Figure 1.2.9 The infrared spectrum of ethanol.

Solution

Peak	Wavenumber (cm^{-1})	Wavenumber is in the range of absorption for
A	3391	O–H bond in alcohols
B	2981	C–H bond
C	1102 and 1055	C–O bond in alcohols

The spectra of even simple molecules with only one functional group will have so many absorption bands that it is not feasible to try to assign every band in the IR spectrum. Instead, look for obvious bands in the region from 4000 to 1300 cm^{-1}. This will help you to determine the presence of specific bonds that indicate particular functional groups. The flow chart in figure 1.2.10 may be helpful in developing habits for analysing infrared spectra.

Infrared spectra may be complex, but modern infrared spectrophotometers assist identification by providing computerized analysis and presentation of data. Characteristic spectra for thousands of compounds have been produced and stored in databases. The spectrum of an unknown compound can quickly be compared to this reference library of spectra. Even if the unknown compound is a new, previously unrecorded one, comparing its infrared spectrum with those in libraries of characteristic absorption peaks can provide information about possible functional groups and sections of the molecule.

Infrared spectroscopy is a very powerful tool that can be applied to a large range of samples. It can be used to identify the products of organic synthesis reactions. Consider the oxidation of an alcohol to a ketone. If this reaction has

CHEM COMPLEMENT

Increasing degradability

Plastic packaging generates a huge amount of waste. One approach to the problem of the disposal of plastic packaging is to make plastics that are biodegradable or photodegradable. Photodegradable plastics require the inclusion of light-sensitive additives. The carbonyl group (C=O) strongly absorbs infrared radiation (1680–1750 cm^{-1}), so if this group is incorporated into polymer chains used to produce plastic packaging, the items will absorb sunlight and degrade relatively quickly.

been successful, the product will show a carbonyl (C=O) band but no hydroxyl (O–H) band. If no carbonyl band is present, the experiment was not successful. If both carbonyl and hydroxyl bands are present, the oxidation may have progressed further to a carboxylic acid, or it is possible that the product is not pure and there is still alcohol present.

Infrared spectroscopy is often used in conjunction with other techniques such as UV spectroscopy, chromatography, mass spectroscopy and nuclear magnetic resonance spectroscopy to determine the structure of a substance. Applications of infrared spectroscopy include identifying narcotics, identifying compounds in forensic testing, analysing fuels for octane ratings, and determining the structure of naturally occurring substances that may be of use in the pharmaceutical industry.

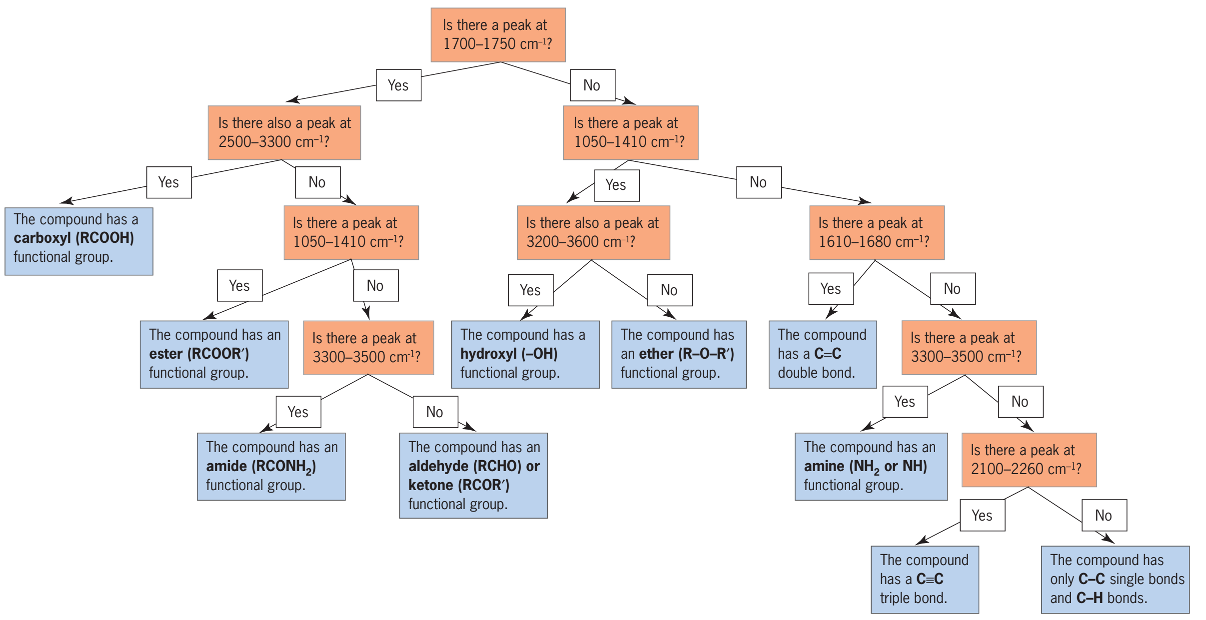


Figure 1.2.10 Flow chart for analysing an infrared spectrum.

Section 1.2 Exercises

1 An infrared spectrometer is used for the analysis of organic compounds. Describe the effect that the passage of infrared radiation has on an organic compound.

2 In several stages, draw an SO_2 molecule as it undergoes:

a a symmetrical stretch

b an asymmetrical stretch

c a bending vibration.

3 Calculate the wavenumber of infrared radiation with the following wavelengths. (Hint: convert the wavelength to cm first.)

a 2×10^{-5} m

b 8×10^{-6} m

c 2.5×10^{-6} m

4 Describe the operating principles of a double-beam infrared spectrometer.

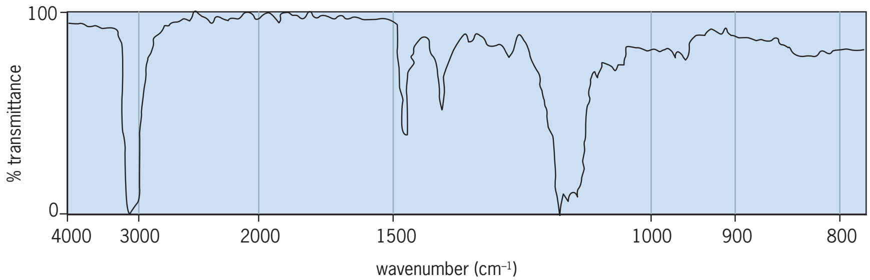
5 Explain why for infrared analysis the sample is placed in a cell, or between discs, of solid sodium chloride, rather than glass or plastic.

6 Describe the location (in terms of the wavenumber) of two peaks that you would expect to find on the infrared spectrum of a sample of propanol.

7 There is one peak that you would expect to occur in all hydrocarbons, that corresponds to C–H. Stating wavenumbers, identify the region in which you would find this peak.

8 The infrared absorption spectrum of an organic compound is shown below.

Use the information in table 1.2.3 to answer these questions.



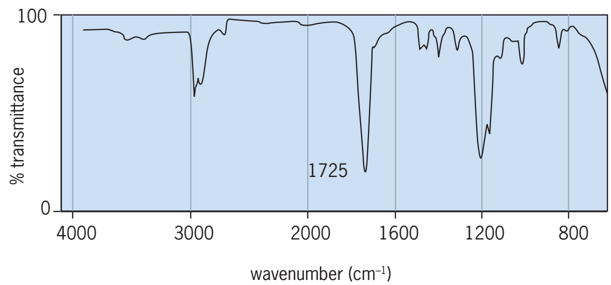
a **i** Suggest one functional group that is present in the compound.

ii Identify one functional group that is not present in the compound.

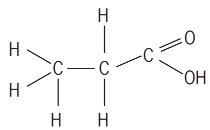
b **i** Stating wavenumbers, identify the region of the spectrum known as the fingerprint region.

ii Describe how this region is used in compound identification.

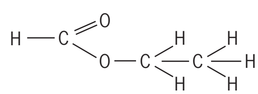
9 The infrared absorption spectrum of an organic compound and two possible structures for the compound are shown below.



A



B



The compound is known to be either A, propanoic acid (CH_3CH_2COOH), or B, ethyl methanoate ($HCOOCH_2CH_3$). Using information from the spectrum and table 1.2.3, identify which compound it is. Explain your choice.