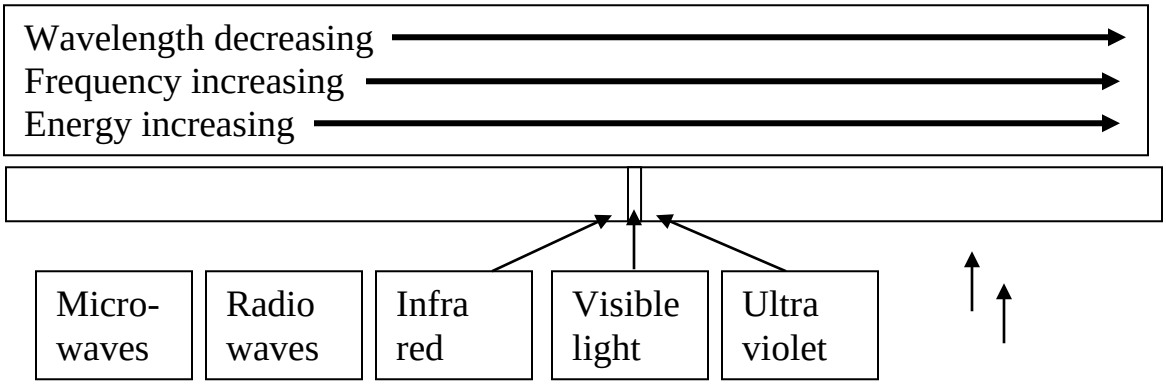
Spectroscopy and Chromatography

Introduction

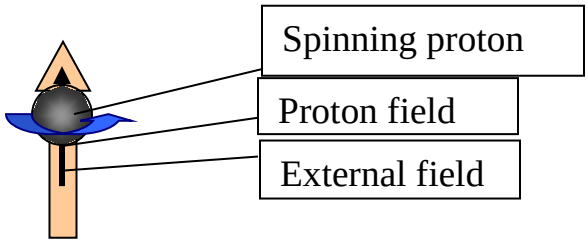
Visible light is one very small part of the electromagnetic spectrum. The different properties of the various types of radiation depend upon their wavelength. The diagram below shows a crude illustration of the various types of radiation of relevance to chemists



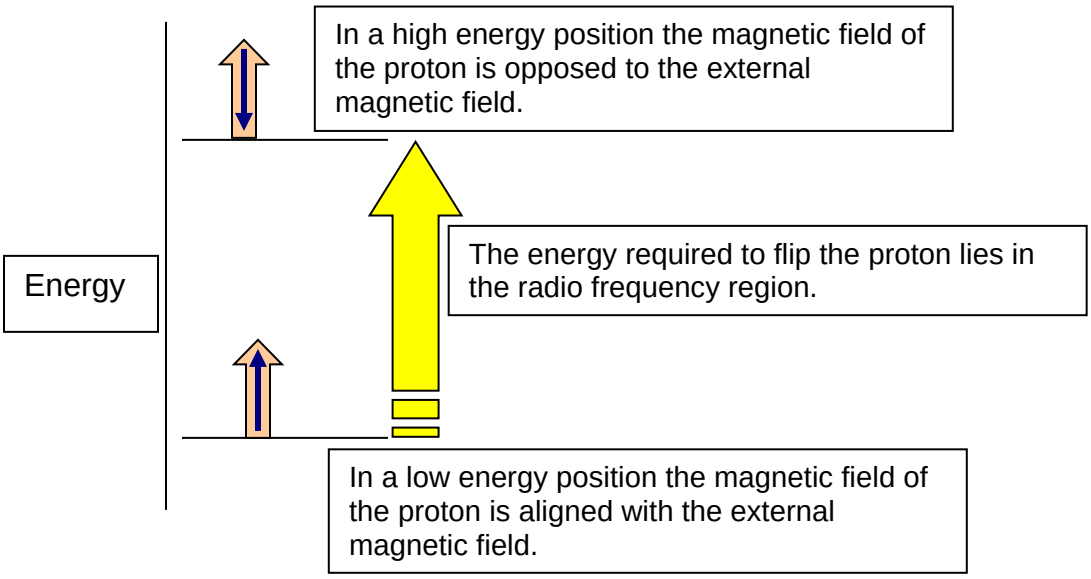
In the Unit 2 section on Spectroscopy the use of **infra red spectroscopy** and **mass spectroscopy** in analysis were looked at. The use of infra red spectroscopy to determine the extent of a reaction involving a change in functional group was also examined. Knowledge and understanding of these aspects are included in this topic of Unit 4.

Nuclear Magnetic Resonance Spectroscopy

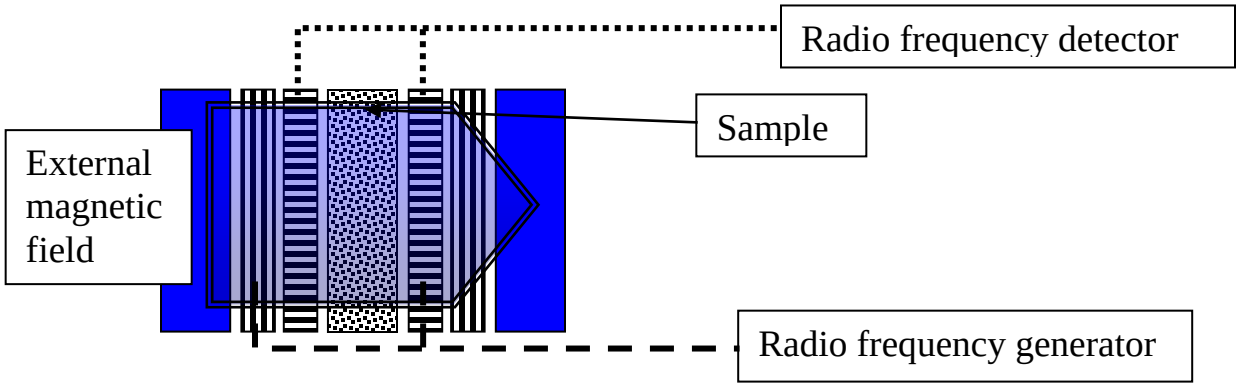
Hydrogen atoms can be detected using this sort of spectrometry.
Any spinning charge generates a magnetic field, so the protons in a nucleus have a magnetic field. If there are two protons in a nucleus they will have opposite spins so the magnetic fields cancel. Nay nucleus with an even number of protons will have no overall magnetic field, but a nucleus with an odd number of protons will have a resultant magnetic field.
When a nucleus with a resultant magnetic field is placed in a strong magnetic field it will align itself with that field.



If the proton supplied with sufficient energy it can flip to a position opposing the external field.
The energy required to do this lies in the radio frequency region of the electromagnetic spectrum.



The actual energy required depends upon the exact environment on the proton. In nuclear magnetic resonance, **NMR**, spectroscopy a substance is placed in a strong magnetic field and subjected to a range of radio frequencies. The point at which a particular radio frequency is absorbed will depend upon the environments of the protons present in that substance.



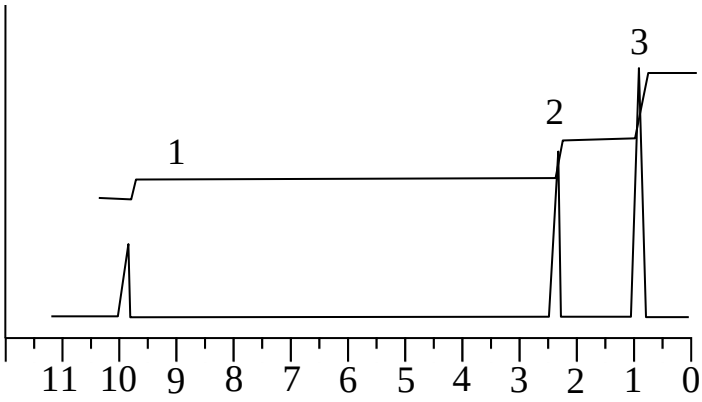
The detector will show which radio frequencies are absorbed. The system is calibrated, usually using the compound **tetramethylsilane, $Si(CH_3)_4$,** as the 0 point and then other frequencies compared to this as shift values.
Selected shift values are given in the table below.

Hydrogen environment	shift
C**H**$_3$-R	0.9
R-C**H**$_2$-R	1.3
R$_3$C**H**	2.0
-C=O-C**H**$_3$-R	2.3
R-C**H**$_2$-OH	3.6
RO**H**	4.5
-C**H**O	9.5

NMR spectra.

The number of protons that can be found in each environment are given by area under the line and defined by the integration trace.

A simplified nmr for propanal is shown below.



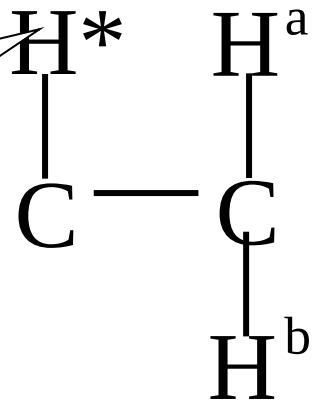
The peak at 9.9 shows -C**H**O

The peak at 2.3 shows -C=O-C**H**$_3$-R

The peak at 0.9 shows C**H**$_3$-R

High resolution NMR spectrum give further information about the proton environment.

The field experienced by this proton will be affected by the two protons on the adjacent carbon.

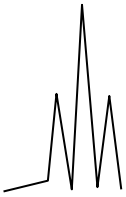


These protons can affect the field at H* according to whether they are aligned with the field or against it.

The effects are shown in the table below;

a	b	Alignment	Number with this alignment
↑	↑	2 against field	1
↑	↓	1 with field 1against field	2
↓	↑	1 with field 1against field	
↓	↓	2 with field	1

This means that when looked at in high resolution the following pattern is seen

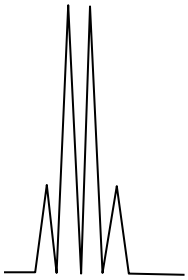


A triplet at ratio 1:2:1 indicates that there are two protons on the adjacent carbon

If there are three protons on the adjacent carbon

a	b	c	Alignment	Number with this alignment
↑	↑	↑	3 against the field	1
↑	↑	↓	2 against the field 1 with the field	3
↓	↑	↑	2 against the field 1 with the field	
↑	↓	↑	2 against the field 1 with the field	
↓	↓	↑	1 against the field 2 with the field	3
↓	↑	↓	1 against the field 2 with the field	
↑	↓	↓	1 against the field 2 with the field	
↓	↓	↓	3 with the field	1

A quadruplet at ratio 1:3:3:1 indicates that there are three protons on the adjacent carbon



Uses of NMR

Clearly NMR is important for chemical analysis. It also has useful applications in medicine.

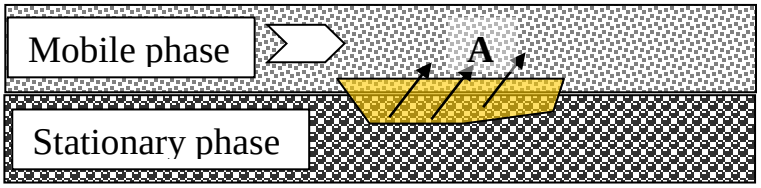
The principle of nuclear magnetic resonance is used in Magnetic Resonance Imaging, MRI, body scanners which detect the protons in water molecules in the body. This process, unlike the use of X-rays is thought to be completely harmless to patients.

Nuclear magnetic resonance can be used to determine the purity of pharmaceutical products.

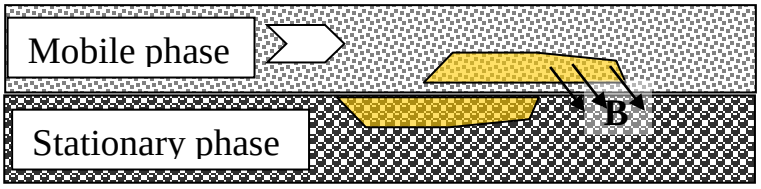
Chromatography

Simple paper chromatography can be used to separate a mixture of dyes.
The principle on which this works are also useful for more sophisticated techniques.

Essentially any form of chromatography used a fixed material (stationary phase) and moving substance (mobile phase). The separation occurs due to the equilibrium between the components in the mixture and the stationary and mobile phases.



The low concentration of the material in the liquid (at A) causes the material to dissolve

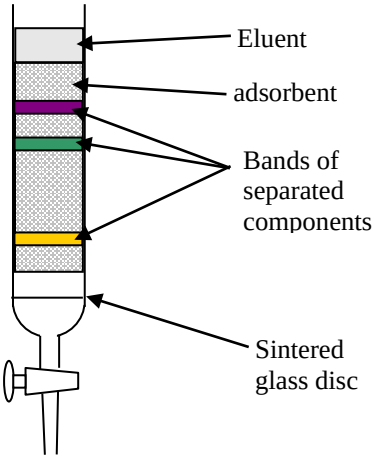


The liquid carries the dissolved material forward. The low concentration of the material at B causes the material to be adsorbed into the stationary phase.

The process continues in this way, the rate of movement determined by the equilibrium movement which depends upon the strength of the interaction of the material with the stationary phase and its solubility in the solvent in the mobile phase.

Column chromatography

One version of this technique is column chromatography. In this process a column is packed with an adsorbent solid, such as alumina. The mixture is then placed in the top of the column so that it is adsorbed onto the surface of the solid. The solvent (or **eluent**) is then poured into the top and allowed to trickle through the column.
Partition of the solutes between the moving solvent and the stationery phase takes place. The rate at which the solute moves down the column depends upon its partition coefficient.



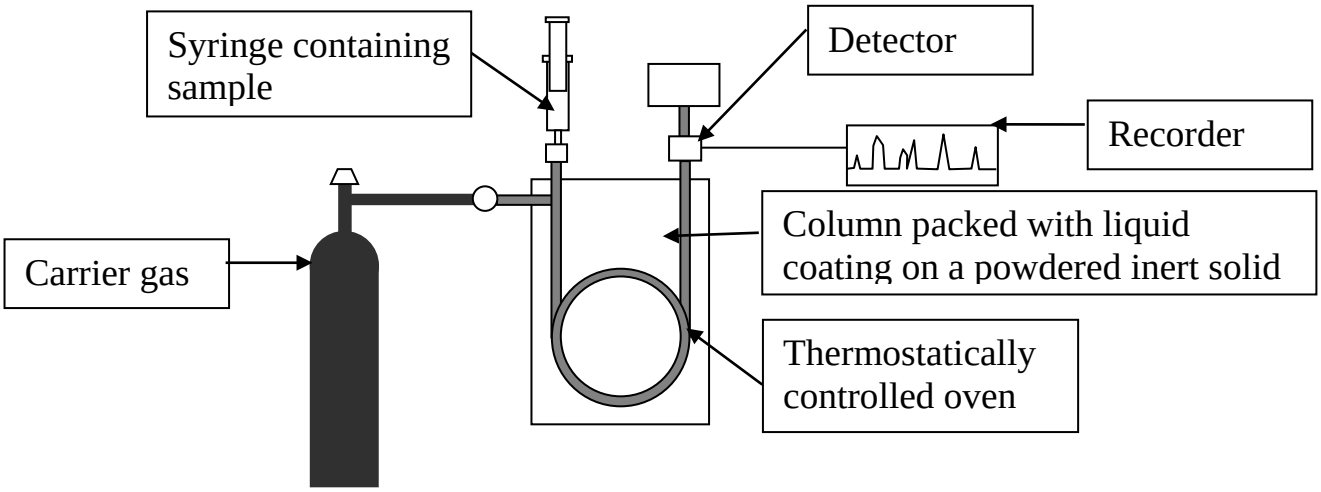
If the component is coloured, it is clear when it emerged from the column. If can be collected and the solvent evaporated to obtain the pure substance. If the substance is colourless, there are other ways of detecting their presence, for example certain materials glow in ultra-violet light.

High-Performance Liquid Chromatography

The effectiveness of column chromatography can be improved by using a very fine powder as the stationary phase. Under these circumstances however gravitation is insufficient to drive the solvent through the system, so a pressure is used to drive the materials through the column. This process is called high-performance liquid chromatography, HPLC.
The HPLC technique is used to separate mixtures and the components can then be analysed.

Gas-Liquid Chromatrography

In gas-liquid chromatography the mobile phase is an inert gas and the stationary phase a liquid coating on a powdered inert solid. The powder fills a coiled tube which about 2mm in diameter and up to 10m long. The coiled tube is situated in an oven which controls its temperature.



The vaporized sample is injected into the carrier gas which moves through the tube at a constant rate. Volatile components of a mixture are carried through the tube fast, while those that are more soluble in the mobile phase take longer to pass through the tube. The time a component spends going through the tube is called the **retention time**.
The area under each peak from the recorder is a measure of the amount of that component.