

# CIE Chemistry A-Level

## Topic 22 - Analytical Techniques

### Flashcards

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# What is chromatography? (A level only)



# What is chromatography? **(A level only)**

A process used to separate a mixture of substances.



In thin-layer chromatography (TLC), what are the different phases?  
**(A level only)**



In thin-layer chromatography (TLC), what are the different phases? **(A level only)**

Mobile phase - solvent.

Stationary phase - layer of silica gel or alumina on a piece of glass.



After TLC, how can the  $R_f$  value be calculated?  
**(A level only)**



After TLC, how can the R<sub>f</sub> value be calculated?  
**(A level only)**

R<sub>f</sub> value is the retention factor value

$$R_f = \frac{\text{distance travelled by component}}{\text{distance travelled by solvent front}}$$



# Why are substances separated during TLC? **(A level only)**





# Why are substances separated during TLC?

**(A level only)**

Substances separate because different compounds have different solubilities in the mobile phase and different attractions to the stationary phase.



What are the different phases in  
gas-liquid chromatography (GC)?  
**(A level only)**



What are the different phases in gas-liquid chromatography (GC)? **(A level only)**

- Mobile phase - inert carrier gas (e.g. helium).
- Stationary phase - liquid with a high boiling point that is adsorbed into a solid.



What does the term retention time mean  
in relation to GC?  
**(A level only)**



What does the term retention time mean in relation to GC? **(A level only)**

The amount of time taken for a sample to travel from the injector to the detector.



How does boiling point affect the retention time of a compound in GC?  
**(A level only)**



How does boiling point affect the retention time of a compound in GC? **(A level only)**

Compounds with higher boiling points will condense sooner in the column so the retention time will be longer.



How does solubility in the liquid stationary phase affect retention time of a compound in GC?  
**(A level only)**





How does solubility in the liquid stationary phase affect retention time of a compound in GC?

**(A level only)**

More soluble compounds will have longer retention times as they spend less time in the carrier gas mobile phase.



How does temperature affect the retention time of a compound in GC?  
**(A level only)**



How does temperature affect the retention time of a compound in GC? **(A level only)**

The higher the temperature, the shorter the retention times of all compounds as the molecules have more kinetic energy.



How can a gas-liquid chromatogram be used to work out the percentage composition of a mixture?  
**(A level only)**



How can a gas-liquid chromatogram be used to work out the percentage composition of a mixture?

**(A level only)**

The area under each peak is the relative amount of each substance. Area is calculated using  $\frac{1}{2} \times \text{base} \times \text{height}$ . This can be converted to a percentage:

$$\text{Percentage composition} = \frac{\text{area under one peak}}{\text{total area under all peaks}} \times 100$$



What happens when infra-red radiation is directed at a compound?



What happens when infra-red radiation is directed at a compound?

Bonds within the molecule absorb specific frequencies of radiation.



What happens when specific frequencies of radiation are absorbed by bonds in a molecule?





What happens when specific frequencies of radiation are absorbed by bonds in a molecule?

The bonds vibrate. This causes the bond to stretch or bend.



What can be identified using peaks on an infra-red spectrum? How?



What can be identified using peaks on an infra-red spectrum? How?

The functional groups within a molecule can be identified by comparing the peaks to known values in a data book.



What is the fingerprint region on an infra-red spectrum?



What is the fingerprint region on an infra-red spectrum?

The region typically between  $1500\text{cm}^{-1}$  and  $500\text{cm}^{-1}$  that contains a complicated series of absorptions. Every compound has a unique fingerprint region.



Briefly describe what happens during  
mass spectrometry  
**(A level only)**



## Briefly describe what happens during mass spectrometry **(A level only)**

A vaporised sample of atoms or molecules is turned into positive ions. The ions are accelerated, deflected by a magnetic field and then detected. This produces a graph with mass to charge ratio ( $m/z$ ) on the x axis and relative abundance on the y axis.



What is the molecular ion ( $M^+$ ) peak on a mass spectrum?  
**(A level only)**





What is the molecular ion ( $M^+$ ) peak on a mass spectrum? **(A level only)**

The peak with the greatest mass to charge ratio. The molecular mass of a compound is equal to the  $m/z$  value of this peak.



What is the  $M^{+1}$  peak on a mass spectrum? What is it caused by?  
**(A level only)**



What is the  $M^{+1}$  peak on a mass spectrum? What is it caused by? **(A level only)**

A tiny peak 1 unit to the right of the molecular ion peak. This is caused by the presence of the  $^{13}\text{C}$  isotope (relative abundance 1.11%).  $^{13}\text{C}$  has one more neutron than  $^{12}\text{C}$  meaning that the relative formula mass is increased by 1.



How can the relative heights of the  $M^+$  and  $M^{+1}$  peaks be used to predict the number of carbon atoms in a molecule?  
**(A level only)**



How can the relative heights of the  $M^+$  and  $M^{+1}$  peaks be used to predict the number of carbon atoms in a molecule? **(A level only)**

$n$  is the number of carbon atoms

$$n = \frac{100}{1.1} \times \frac{\text{abundance of } M^{+1} \text{ ion}}{\text{abundance of } M^+ \text{ ion}}$$



When would an  $M^{+2}$  peak be seen on a mass spectrum? **(A level only)**



When would an  $M^{+2}$  peak be seen on a mass spectrum? **(A level only)**

When a compound contains a chlorine or bromine atom.



Describe how the presence of a chlorine atom in a compound causes an  $M^{+2}$  peak on the mass spectrum  
**(A level only)**





Describe how the presence of a chlorine atom in a compound causes an  $M^{+2}$  peak on the mass spectrum **(A level only)**

In these compounds, chlorine exists as two isotopes:  $^{35}\text{Cl}$  or  $^{37}\text{Cl}$ . Compounds containing the  $^{37}\text{Cl}$  isotope will have a relative formula mass that is 2 units larger than compounds containing the  $^{35}\text{Cl}$  isotope, causing the  $M^{2+}$  peak.



What is the ratio of the peak heights of the  $M^+$  and  $M^{+2}$  peaks on the mass spectrum of a compound containing chlorine? Why?  
**(A level only)**



What is the ratio of the peak heights of the  $M^+$  and  $M^{+2}$  peaks on the mass spectrum of a compound containing chlorine? Why? **(A level only)**

3:1

Chlorine is 3 times more likely to be  $^{35}\text{Cl}$  than  $^{37}\text{Cl}$ .



Describe how the presence of a bromine atom in a compound causes an  $M^{+2}$  peak on the mass spectrum  
**(A level only)**



Describe how the presence of a bromine atom in a compound causes an  $M^{+2}$  peak on the mass spectrum **(A level only)**

Bromine exists as two isotopes:  $^{79}\text{Br}$  or  $^{81}\text{Br}$ .

Compounds containing the  $^{81}\text{Br}$  isotope will have a relative formula mass that is 2 units larger than compounds containing the  $^{79}\text{Br}$  isotope, causing the  $M^{2+}$  peak.



How many molecular peaks will a compound containing three chlorine atoms have?  
**(A level only)**



How many molecular peaks will a compound containing three chlorine atoms have? **(A level only)**

Four molecular peaks. There are two isotopes of chlorine so there are four different combinations:

$$35 + 35 + 35$$

$$35 + 35 + 37$$

$$35 + 37 + 37$$

$$37 + 37 + 37$$



# Describe the formation of fragment ions during mass spectrometry **(A level only)**





Describe the formation of fragment ions during mass spectrometry **(A level only)**

Fragment ions form when an unstable molecular ions break down into a positive ion and an uncharged free radical.



# What is a free radical?

## (A level only)



What is a free radical? **(A level only)**

A species with an unpaired electron.



Why are the free radicals formed during the fragmentation of molecular ions not shown as peaks on the mass spectrum?  
**(A level only)**



Why are the free radicals formed during the fragmentation of molecular ions not shown as peaks on the mass spectrum? **(A level only)**

These free radicals are uncharged. Only charged particles are detected.



How can a fragment ion be identified  
from a mass spectrum?  
**(A level only)**



How can a fragment ion be identified from a mass spectrum? **(A level only)**

Compare the  $m/z$  value of the fragment ion peak with the relative formula masses of possible fragment ions.



Why can  $^{13}\text{C}$  nuclei be used in NMR  
spectroscopy?  
**(A level only)**





# Why can $^{13}\text{C}$ nuclei be used in NMR spectroscopy? (A level only)

$^{13}\text{C}$  nuclei can align with or against a magnetic field. It is less stable to oppose the magnetic field meaning this has higher energy. Energy can be supplied to the nucleus in the form of radio waves and cause it to flip from the more stable alignment to the less stable alignment. This energy change depends on the carbon environment.



# What is a carbon environment? (A level only)



What is a carbon environment? **(A level only)**

The atoms, or groups of atoms, that a carbon atom is bonded to.



# What can be deduced from a carbon-13 NMR spectrum? How? **(A level only)**



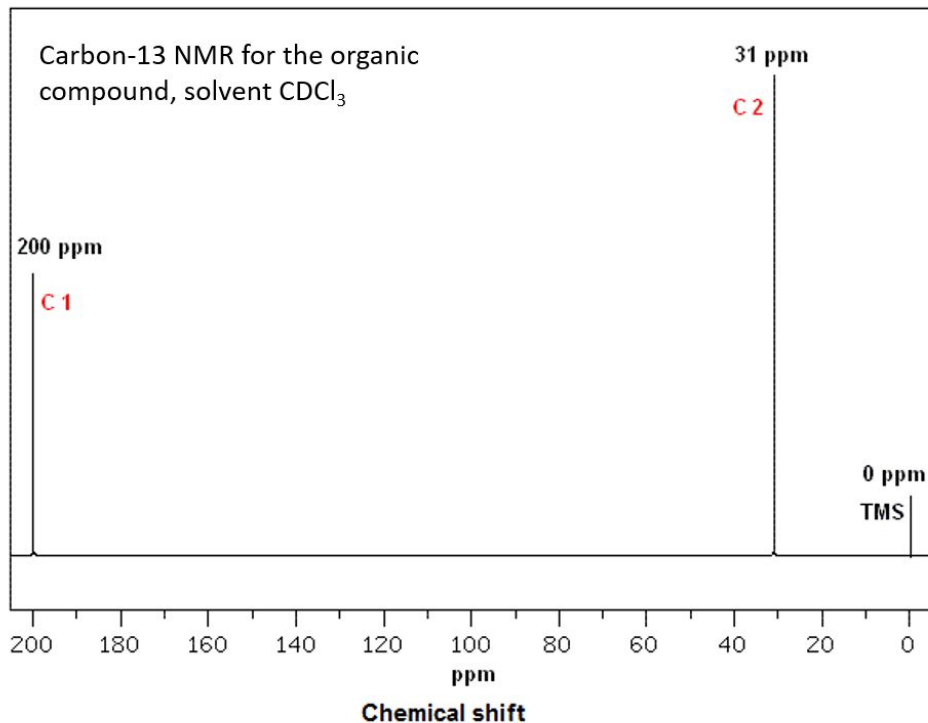
What can be deduced from a carbon-13 NMR spectrum? How? **(A level only)**

Number of different carbon environments = number of peaks on the spectrum.

Types of carbon environments - compare the chemical shift values of the peaks to the data book to identify the carbon environments.



An organic compound contains two carbons and has the  $^{13}\text{C}$  NMR spectrum shown. Determine its structure  
**(A level only)**



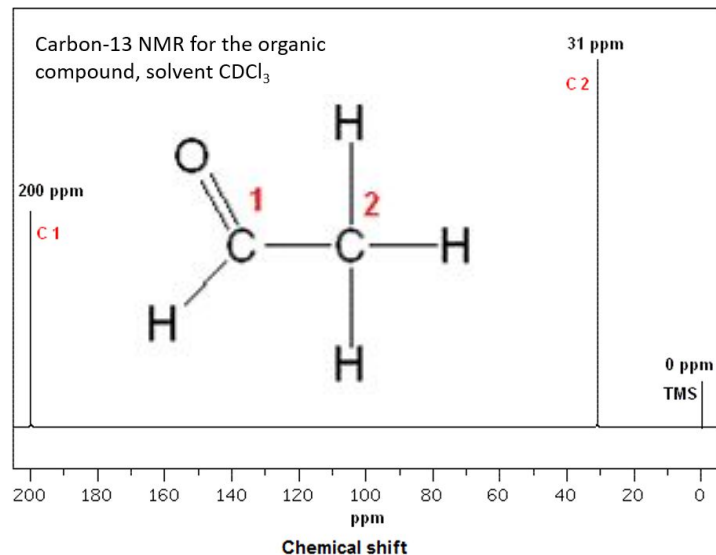
['File:13C NMR ethanal.GIF', Wikimedia Commons](#)

[CC0 1.0](#)



An organic compound contains two carbons and has the  $^{13}\text{C}$  NMR spectrum shown. Determine its structure **(A level only)**

- The compound has 2 carbons.
- There is a peak at 200 ppm meaning the compound must contain  $\text{C}=\text{O}$ .
- The spectrum shows 2 peaks so there are 2 different carbon environments. Both carbons are in different environments.
- The chemical is ethanal.



['File:13C NMR ethanal.GIF'. Wikimedia Commons](#)

[CC0 1.0](#)



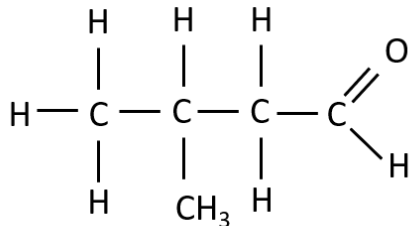
Predict the number of peaks in the  $^{13}\text{C}$   
NMR spectrum for 3-methylbutanal  
**(A level only)**



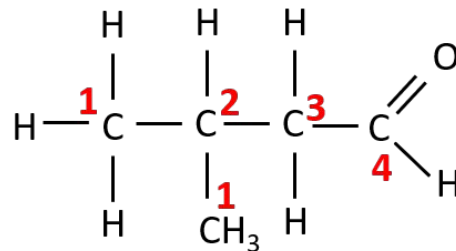


Predict the number of peaks in the  $^{13}\text{C}$  NMR spectrum for 3-methylbutanal (**A level only**)

Structure:



Number the carbon environments:



There are 4 environments so there will be 4 peaks.



# Why can protons be used in NMR spectroscopy? **(A level only)**



# Why can protons be used in NMR spectroscopy? (A level only)

Hydrogen nuclei can align with or against a magnetic field. The direction of this alignment can be flipped using a specific frequency of radio waves (known as resonance condition). This is because there is a difference in the energy of the two alignments. The frequency required for this change depends on the proton environment.



How can a proton environment be identified using a proton NMR spectrum?  
**(A level only)**



How can a proton environment be identified using a proton NMR spectrum? **(A level only)**

Compare the chemical shift values of the peaks to values in the data book.



On a proton NMR spectrum, what does the ratio of the areas under the peaks indicate?  
**(A level only)**



On a proton NMR spectrum, what does the ratio of the areas under the peaks indicate? **(A level only)**

The relative number of protons in each environment.



# What are equivalent protons?

## (A level only)





What are equivalent protons? **(A level only)**

Protons in the same environment. These may be on the same or different carbons.



What does the splitting pattern of peaks  
on a proton NMR spectrum show?  
**(A level only)**



What does the splitting pattern of peaks on a proton NMR spectrum show? **(A level only)**

The number of protons on the adjacent carbon atoms.



Name the first 4 splitting patterns on a  
proton NMR spectrum  
**(A level only)**



Name the first 4 splitting patterns on a proton NMR spectrum **(A level only)**

Singlet (1 peak)

Doublet (2 peaks)

Triplet (3 peaks)

Quartet (4 peaks)



# What is the $n+1$ rule? (A level only)



What is the  $n+1$  rule? **(A level only)**

The number of peaks in the splitting pattern is equal to the number of adjacent protons  $(n) + 1$ .



# When doesn't the $n+1$ rule work? (A level only)





## When doesn't the $n+1$ rule work? (A level only)

- Alcohols - the chemical shift for the hydrogen atom in  $-OH$  is variable and this peak is always a singlet.  $-OH$  doesn't cause splitting in adjacent hydrogens.
- Equivalent hydrogens - protons bonded to the same carbon (protons in the same environment) have no effect on each other in terms of splitting.
- Benzene - the splitting pattern is very complicated (called a multiplet). The peaks for a benzene ring will be found in the range 6.0-9.0 ppm.



What does the peak at 0 ppm on a proton NMR represent?  
**(A level only)**



What does the peak at 0 ppm on a proton NMR represent? **(A level only)**

TMS (tetramethylsilane)



What is TMS used as?  
**(A level only)**



What is TMS used as? **(A level only)**

The standard for chemical shift measurements during NMR spectroscopy.



Why is TMS used as the standard for  
chemical shift measurements in NMR  
spectroscopy?  
**(A level only)**



# Why is TMS used as the standard for chemical shift measurements in NMR spectroscopy? **(A level only)**

- It has 12 hydrogens in the same environment meaning a single strong peak will be produced in proton NMR.
- It contains carbon and hydrogen atoms meaning it can be used in both carbon and proton NMR.
- It contains 1 carbon environment meaning it produced a single peak in  $^{13}\text{C}$  NMR.
- It's non-toxic.
- It's inert so won't react with the compounds under analysis.



What is a deuterated solvent? Why are they used in NMR spectroscopy?  
**(A level only)**





What is a deuterated solvent? Why are they used in NMR spectroscopy? **(A level only)**

A deuterated solvent contains deuterium (an isotope of hydrogen) instead of  $^1\text{H}$ . They are used so that they don't produce a peak on the proton NMR spectrum so the solvent won't affect analysis.



Why are O-H and N-H protons difficult to identify?  
**(A level only)**



Why are O-H and N-H protons difficult to identify?  
**(A level only)**

Their chemical shift values are variable.



# Describe how to identify O-H and N-H protons

## (A level only)



## Describe how to identify O-H and N-H protons (A level only)

1. Run a proton NMR to obtain a spectrum for the compound being analysed.
2. Shake the sample with  $D_2O$ .
3. Run a second NMR and compare the spectra. Any peaks caused by O-H or N-H protons will disappear with  $D_2O$ .



Why does proton exchange occur between an alcohol and  $D_2O$ ? Why does this cause the O-H peak to disappear from the NMR spectrum?

**(A level only)**



Why does proton exchange occur between an alcohol and  $D_2O$ ? Why does this cause the O-H peak to disappear from the NMR spectrum?

**(A level only)**

Alcohols are slightly acidic meaning the hydrogen in the OH group transfers to one of the lone pairs on oxygen in  $D_2O$ . The negative ion formed is likely to collide with  $D_2O$  which will reform the alcohol with an OD group instead of an OH group. Deuterium doesn't produce a peak on the NMR spectrum meaning the peak caused by the O-H proton disappears.

