CAIE Chemistry A-level

Topic 37 - Analytical Techniques

(A level only)

Flashcards

What is chromatography?

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A process used to separate substances in a mixture. Separation of the substance depends on distribution between a mobile phase and a stationary phase.

In thin-layer chromatography (TLC), what are the different phases?

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Mobile phase - solvent.

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

After TLC, how can the Rf value be calculated?

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Rf value is the retention factor value

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

Why are substances separated during TLC?

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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)?

What are the different phases in gas-liquid chromatography (GC)?

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 gas chromatography?

What does the term retention time mean in relation to gas chromatography?

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 gas chromatography?

How does boiling point affect the retention time of a compound in gas chromatography?

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 gas/liquid chromatography?

How does solubility in the liquid stationary phase affect retention time of a compound in gas/liquid chromatography?

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 gas/liquid chromatography?

How does temperature affect the retention time of a compound in gas/liquid chromatography?

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?

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

The area under each peak is the relative amount of each substance. Area is calculated using ½ x base x height. This can be converted to a percentage:

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

Why can ^{13}C nuclei be used in NMR spectroscopy?

Why can ^{13}C nuclei be used in NMR spectroscopy?

^{13}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?

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

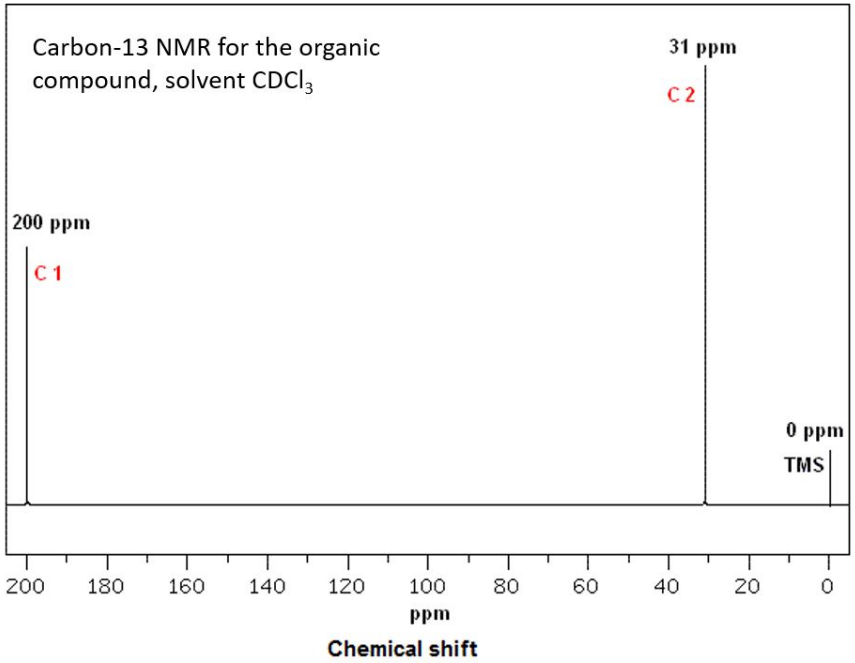
What can be deduced from a carbon-13 NMR spectrum? How?

What can be deduced from a carbon-13 NMR spectrum? How?

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.

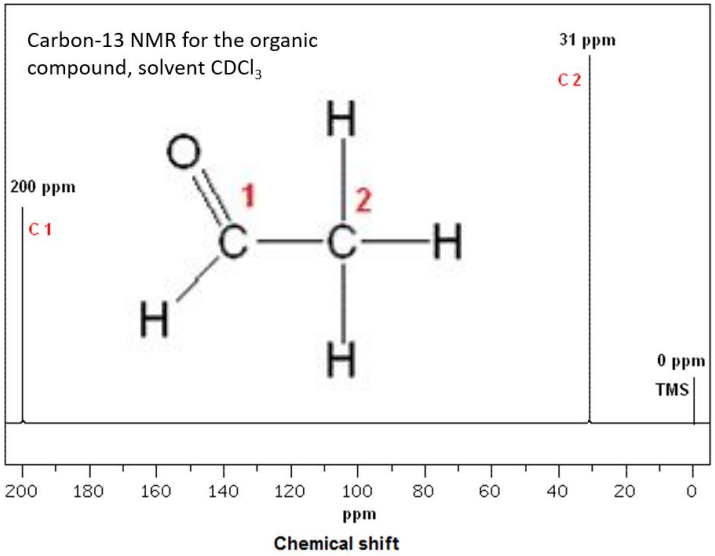
An organic compound contains two carbons and has the ^{13}C NMR spectrum shown. Determine its structure.



'File:13C NMR ethanal.GIF', Wikimedia, Commons CC0 1.0

An organic compound contains two carbons and has the ^{13}C NMR spectrum shown. Determine its structure.

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



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Predict the number of peaks in the ^{13}C NMR spectrum for 3-methylbutanal

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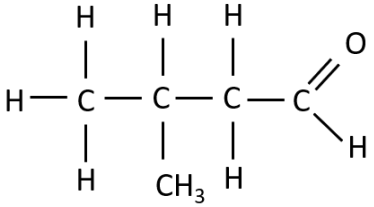
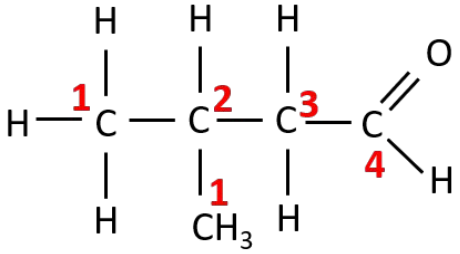
Structure:



Number the carbon environments:



There are 4 environments so there will be 4 peaks.

Why can protons be used in NMR spectroscopy?

Why can protons be used in NMR spectroscopy?

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?

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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?

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The relative number of protons in each environment.

What are equivalent protons?

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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?

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The number of protons on the adjacent carbon atoms.

Name the first four splitting patterns on a proton NMR spectrum

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Singlet (1 peak)

Doublet (2 peaks)

Triplet (3 peaks)

Quartet (4 peaks)

What is the n+1 rule?

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The number of peaks in the splitting pattern is equal to the number of adjacent protons (n) plus one.

When doesn't the n+1 rule work?

When doesn't the n+1 rule work?

- 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?

What does the peak at 0 ppm on a proton NMR represent?

TMS (tetramethylsilane)

What is TMS used as?

What is TMS used as?

The standard for chemical shift measurements during NMR spectroscopy.

Why is TMS used as the standard for chemical shift measurements in NMR spectroscopy?

Why is TMS used as the standard for chemical shift measurements in NMR spectroscopy?

- 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}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?

What is a deuterated solvent? Why are they used in NMR spectroscopy?

A deuterated solvent contains deuterium (an isotope of hydrogen) instead of ^{1}H. They are used so that they don't produce a peak on the proton NMR spectrum. This means the solvent will not interfere with the analysis.

Why are O-H and N-H protons difficult to identify?

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Their chemical shift values are variable.

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

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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?

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?

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.