# Uncertainty and error in measurement

RANDOM UNCERTAINTIES AND SYSTEMATIC ERRORS

Quantitative chemistry involves measurement. A measurement is a method by which some quantity or property of a substance is compared with a known standard. If the instrument used to take the measurements has been calibrated wrongly or if the person using it consistently misreads it then the measurements will always differ by the same amount. Such an error is known as a **systematic error**. An example might be always reading a pipette from the sides of the meniscus rather than from the middle of the meniscus.

correct   incorrect
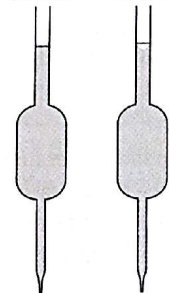
a systematic error will be introduced if a pipette is read incorrectly
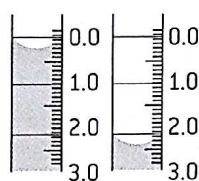
systematic errors may cancel out when a difference in two readings is taken $\Delta V = 2.0 \, cm^3$ whether or not the burette is read

Random uncertainties occur if there is an equal probability of the reading being too high or too low from one measurement to the next. These might include variations in the volume of glassware due to temperature fluctuations or the decision on exactly when an indicator changes colour during an acid–base titration.

PRECISION AND ACCURACY

Precision refers to how close several experimental measurements of the same quantity are to each other. **Accuracy** refers to how close the readings are to the true value. This may be the standard value, or the literature or accepted value. A measuring cylinder used to measure exactly 25 cm³ is likely to be much less accurate than a pipette that has been carefully calibrated to deliver exactly that volume. It is possible to have very precise readings which are inaccurate due to a systematic error. For example all the students in the class may obtain the same or very close results in a titration but if the standard solution used in all the titrations had been prepared wrongly beforehand the results would be inaccurate due to the systematic error. Because they are always either too high or too low systematic errors cannot be reduced by repeated readings. However random errors can be reduced by repeated readings because there is an equal probability of them being high or low each time the reading is taken. When taking a measurement it is usual practice to report the reading from a scale as the smallest division or the last digit capable of precise measurement even though it is understood that the last digit has been rounded up or down so that there is a random error or uncertainty of ± 0.5 of the last unit.

SIGNIFICANT FIGURES

Whenever a measurement of a physical quantity is taken there will be a random uncertainty in the reading. The measurement quoted should include the first figure that is uncertain. This should include zero if necessary. Thus a reading of 25.30 °C indicates that the temperature was measured with a thermometer that is accurate to $+ 0.01$ °C. If a thermometer accurate to only ± 0.1 °C was used the temperature should be recorded as 25.3 °C.

Zeros can cause problems when determining the number of significant figures. Essentially zero only becomes significant when it comes *after* a non-zero digit (1,2,3,4,5,6,7,8,9).

000123.4   0.0001234   1.0234   1.2340

zero not a significant figure values quoted to 4 s.f.   zero is a significant figure values quoted to 5 s.f.

Zeros after a non-zero digit but before the decimal point may or may not be significant depending on how the measurement was made. For example 123 000 might mean exactly one hundred and twenty three thousand or one hundred and twenty three thousand to the nearest thousand. This problem can be neatly overcome by using scientific notation.

1.23000×10^6 quoted to six significant figures

1.23×10^6 quoted to three significant figures.

Calculations

1. When adding or subtracting it is the number of decimal places that is important. Thus when using a balance which measures to ± 0.01 g the answer can also be quoted to two decimal places which may increase or decrease the number of significant figures.

   e.g.   7.10 g   +   3.10 g   =   10.20 g
           3 s.f.   3 s.f.   4 s.f.

           22.36 g   −   15.16 g   =   7.20 g
           4 s.f.   4 s.f.   3 s.f.

2. When multiplying or dividing it is the number of significant figures that is important. The number with the least number of significant figures used in the calculation determines how many significant figures should be used when quoting the answer.

   e.g.   When the temperature of 0.125 kg of water is increased by 7.2 °C

           the heat required
           $= 0.125 \, kg \times 7.2 \, °C \times 4.18 \, kJ \, kg^{-1} \, °C^{-1}$
           $= 3.762 \, kJ$

   Since the temperature was only recorded to two significant figures the answer should strictly be given as 3.8 kJ.

Uncertainty in calculated results and graphical techniques

ABSOLUTE AND PERCENTAGE UNCERTAINTIES

When making a single measurement with a piece of apparatus the absolute uncertainty and the percentage uncertainty can both be stated relatively easily. For example consider measuring 25.0 cm³ with a 25 cm³ pipette which measures to ± 0.1 cm³. The absolute uncertainty is 0.1 cm³ and the percentage uncertainty is equal to:

$$\frac{0.1}{25.0} \times 100 = 0.4\%$$

If two volumes or two masses are simply added or subtracted then the absolute uncertainties are added. For example suppose two volumes of 25.0 cm³ ± 0.1 cm³ are added. In one extreme case the first volume could be 24.9 cm³ and the second volume 24.9 cm³ which would give a total volume of 48.8 cm³. Alternatively the first volume might have been 25.1 cm³ which when added to a second volume of 25.1 cm³ gives a total volume of 50.2 cm³. The final answer therefore can be quoted between 48.8 cm³ and 50.2 cm³, that is, 50.0 cm³ ± 0.2 cm³.

When using multiplication, division or powers then percentage uncertainties should be used during the calculation and then converted back into an absolute uncertainty when the final result is presented. For example, during a titration there are generally four separate pieces of apparatus, each of which contributes to the uncertainty.

e.g. when using a balance that weighs to ± 0.001 g the uncertainty in weighing 2.500 g will equal

$$\frac{0.001}{2.500} \times 100 = 0.04\%$$

Similarly a pipette measures 25.00 cm³ ± 0.04 cm³.

The uncertainty due to the pipette is thus

$$\frac{0.04}{25.00} \times 100 = 0.16\%$$

Assuming the uncertainty due to the burette and the volumetric flask is 0.50% and 0.10% respectively the overall uncertainty is obtained by summing all the individual uncertainties:

Overall uncertainty = 0.04 + 0.16 + 0.50 + 0.10
                    = 0.80% ≃ 1.0%

Hence if the answer is 1.87 mol dm⁻³ the uncertainty is 1.0% or 0.0187 mol dm⁻³.

The answer should be given as 1.87 ± 0.02 mol dm⁻³.

If the generally accepted 'correct' value (obtained from the data book or other literature) is known then the total error in the result is the difference between the literature value and the experimental value divided by the literature value expressed as a percentage. For example, if the 'correct' concentration for the concentration determined above is 1.90 mol dm⁻³ then:

$$\text{the total error} = \frac{(1.90 - 1.87)}{1.90} \times 100 = 1.6\%$$

GRAPHICAL TECHNIQUES

By plotting a suitable graph to give a straight line or some other definite relationship between the variables, graphs can be used to predict unknown values. There are various methods to achieve this. They include measuring the intercept, measuring the gradient, extrapolation and interpolation. **Interpolation** involves determining an unknown value within the limits of the values already measured. **Extrapolation** (see example on page 38) requires extending the graph to determine an unknown value which lies outside the range of the values measured. If possible manipulate the data to produce a straight line graph. For example, when investigating the relationship between pressure and volume for a fixed mass of gas a plot of P against V gives a curve whereas a plot of P against 1/V will give a straight line. Once the graph is in the form of y = mx + c then the values for both the gradient (m) and the intercept (c) can be determined.

sketch graph of pressure against volume for a fixed mass of gas at a constant temperature

sketch graph of pressure against the reciprocal of volume for a fixed mass of gas at a constant temperature
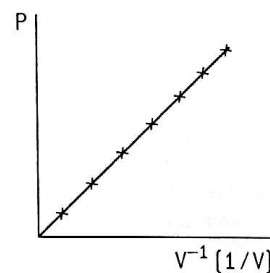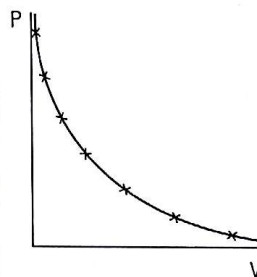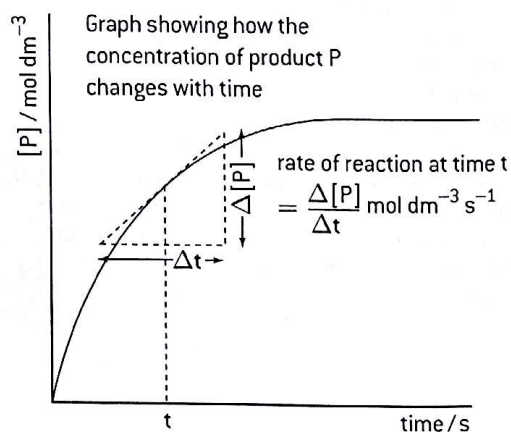

Note that a sketched graph has labelled but unscaled axes and is used to show qualitative trends. Drawn graphs have labelled and scaled axes and are used in quantitative measurements.

The following points should be observed when drawing a graph.

- Plot the independent variable on the horizontal axis and the dependent variable on the vertical axis.
- Choose appropriate scales for the axes.
- Use Standard International (SI) units wherever possible.
- Label each axis and include the units.
- Draw the line of best fit.
- Give the graph a title.

Measuring a gradient from a graph

Graph showing how the concentration of product P changes with time

rate of reaction at time t
$= \dfrac{\Delta[P]}{\Delta t}$ mol dm⁻³ s⁻¹

Analytical techniques

INFORMATION FROM DIFFERENT ANALYTICAL TECHNIQUES

The classic way to determine the structure of an organic compound was to determine both its empirical formula and relative molar mass experimentally, then deduce the nature of the functional groups from its chemical reactivity. However, modern well-equipped laboratories now employ a variety of instrumental techniques, which if used in combination are able to unambiguously determine the exact structural formula. They can also be used to determine the composition of the components in a mixture and to determine purity. These techniques are becoming ever more refined and some of them (e.g. mass spectrometry) can be used on extremely small samples. Before analysis can usually take place it is important to separate any mixture into its individual components – hence the need for chromatography. Often information is not obtained from a single technique but from a combination of several of them. Some examples are:

- Infrared spectroscopy – organic structural determination, information on the strength of bonds, information about the secondary structure of proteins, measuring the degree of unsaturation of oils and fats, and determining the level of alcohol in the breath.
- Mass spectrometry – organic structural determination, isotopic dating (e.g. ^{14}C dating).
- Proton nuclear magnetic resonance spectroscopy (^1H NMR) – organic structural determination, body scanning (known as MRI).
- Chromatography – drug testing in the blood and urine, food testing, and forensic science.

## INDEX OF HYDROGEN DEFICIENCY (IHD)

Once the molecular formula of a compound is known the index of hydrogen deficiency can be calculated. This used to be known as the degree of unsaturation. A non-cyclic hydrocarbon that contains only single bonds contains the maximum number of hydrogen atoms and has the general formula $C_nH_{(2n+2)}$. If any of the bonds are replaced by double or triple bonds or the compound is cyclic then the number of hydrogen atoms falls (i.e. there is a deficiency in the number of hydrogen atoms). The amount of the deficiency therefore gives useful information about the molecule and will assist in determining the number and types of different possible isomers.

The IHD for a hydrocarbon with x carbon atoms and y hydrogen atoms, C_xH_y is given by :

$$IHD = \frac{(2x + 2 - y)}{2}$$

where each double bond and each ring counts as one IHD and each triple bond counts as two IHD.

For example, hexane C_6H_{14} has an IHD equal to $\frac{(12 + 2 - 14)}{2} = 0$. This would be expected as hexane is a saturated hydrocarbon. If however a compound has a molecular formula of C_6H_{12} its IHD is $\frac{(12 + 2 - 12)}{2} = 1$. This means that the compound could contain one double bond and be an isomer of hexene or it could be a cyclic compound.

hexane
C_6H_{14} IHD = zero

hex-2-ene and hex-3-ene
C_6H_{12} IHD = 1

cyclohexane
C_6H_{12} IHD = 1
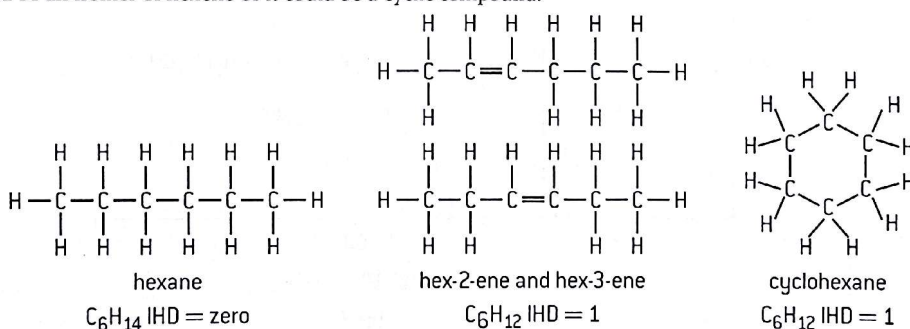
Determining the IHD becomes a little more complicated if elements other than carbon and hydrogen are present in the compound. In this case:

Oxygen and sulfur atoms (O and S) do not affect the IHD.

Halogens (F, Cl, Br, I) are treated like H atoms (i.e. $CHCl_3$ has the same IHD as CH_4).

For each N, add one to the number of C and one to the number of H (i.e. CH_5N has the same IHD as C_2H_6).

THE ELECTROMAGNETIC SPECTRUM

Modern spectroscopic techniques utilize different parts of the electromagnetic spectrum. The electromagnetic spectrum has already been described in Topic 2 – *Atomic structure*. You should be familiar with the relationship $c = \lambda\nu$ and know the different regions of the spectrum.

The electromagnetic spectrum

Wavelength / m	10^{-10} 10^{-9} 10^{-8} 10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^{0} 10^{1} 10^{2} 10^{3}
Frequency / MHz	3×10^{10} 3×10^{8} 3×10^{6} 3×10^{4} 3×10^{2} 3
Type of radiation	X-ray γ-rays ultraviolet visible infrared microwaves radio waves
Type of transition	inner electrons outer electrons molecular vibrations molecular rotations nuclear spin

← increasing energy →

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Spectroscopic identification of organic compounds – MS

MASS SPECTROMETRY

The principles of mass spectroscopy and its use to determine relative atomic masses have already been explained in Topic 2 – *Atomic structure*. It can be used in a similar way with organic compounds. However in addition to giving the precise molecular mass of the substance, mass spectroscopy gives considerable information about the actual structure of the compound from the fragmentation patterns.

When a sample is introduced into the machine the vaporized sample becomes ionized to form the molecular ion $M^+(g)$. Inside the mass spectrometer some of the molecular ions break down to give fragments, which are also deflected by the external magnetic field and which then show up as peaks on the detector. By looking at the difference in mass from the parent peak it is often possible to identify particular fragments,

e.g. $(M_r - 15)^+ = $ loss of CH_3

$(M_r - 17)^+ = $ loss of OH

$(M_r - 18)^+ = $ loss of H_2O

$(M_r - 28)^+ = $ loss of C_2H_4 or CO

$(M_r - 29)^+ = $ loss of C_2H_5 or CHO

$(M_r - 31)^+ = $ loss of CH_3O

$(M_r - 45)^+ = $ loss of $COOH$

This can provide a useful way of distinguishing between structural isomers.

The mass spectra of propan-1-ol and propan-2-ol both show a peak at 60 due to the molecular ion $C_3H_8O^+$. However, the mass spectrum of propan-1-ol shows a strong peak at 31 due to the loss of $-C_2H_5$, which is absent in the mass spectrum of propan-2-ol. There is a strong peak at 45 in the spectrum of propan-2-ol as it contains two different methyl groups, which can fragment.

Mass spectrum of propan-1-ol $CH_3 - CH_2 - CH_2 - OH$
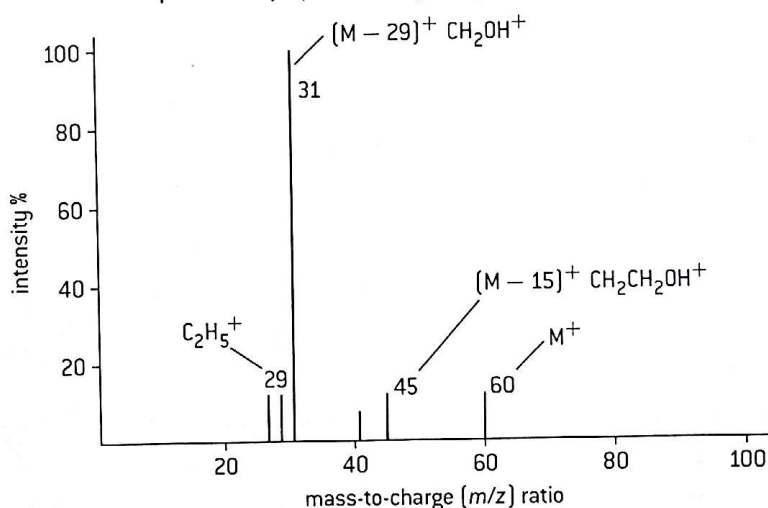
Mass spectrum of propan-2-ol $CH_3 - \overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - CH_3$

MEASUREMENT, DATA PROCESSING AND ANALYSIS
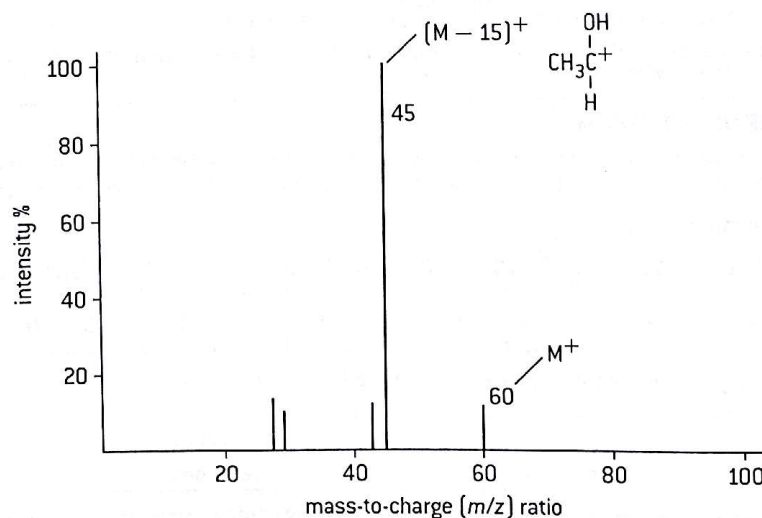
Spectroscopic identification of organic compounds – IR and ¹H NMR
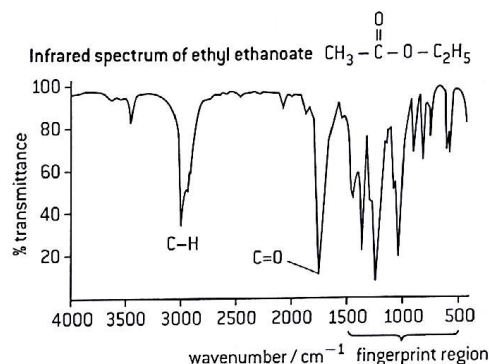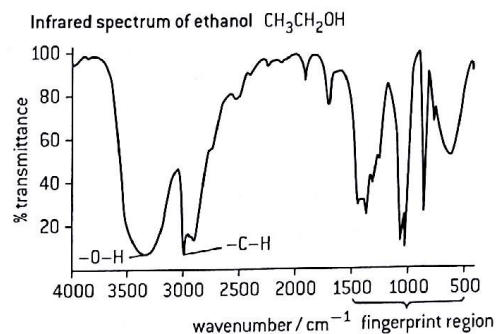
INFRARED SPECTROSCOPY

When molecules absorb energy in the infrared region of the spectrum they vibrate (i.e. the bonds stretch and bend). The precise value of the energy they absorb depends on the particular bond and to a lesser extent on the other groups attached to the two atoms forming the bond. When infrared radiation is passed through a sample the spectrum shows the characteristic absorptions, which confirm that a particular bond is present in the molecule. Some absorptions, e.g. those due to C–H, are not particularly useful, as they are shown by most organic compounds. However others give a very clear indication of a particular functional group.

In addition to these particular absorptions, infrared spectra also possess a 'fingerprint' region. This is a characteristic pattern between about 1400–400 cm⁻¹, which is specific to a particular compound. It is often possible to identify an unknown sample by comparing the fingerprint region with a library of spectra of known compounds.

A simplified correlation chart

Bond	Wavenumber / cm⁻¹
C–Cl	600–800
C–O	1050–1410
C=C	1620–1680
C=O	1700–1750
C≡C	2100–2260
O–H (in carboxylic acids)	2500–3000
C–H	2850–3090
O–H (in alcohols)	3200–3600

Wavenumber is the reciprocal of wavelength.

Infrared spectrum of ethanol CH_3CH_2OH

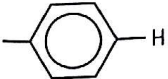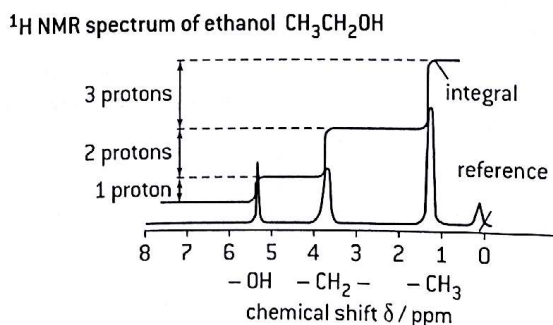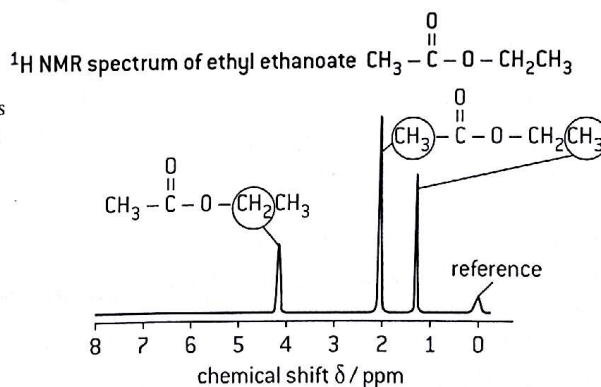Infrared spectrum of ethyl ethanoate $CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5$

PROTON NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (¹H NMR)

Whereas infrared spectroscopy gives information about the types of bonds in a molecule, ¹H NMR spectroscopy provides information on the chemical environment of all the hydrogen atoms in the molecule. The nuclei of hydrogen atoms possess spin and can exist in two possible states of equal energy. If a strong magnetic field is applied the spin states may align themselves either with the magnetic field, or against it, and there is a small energy difference between them. The nuclei can absorb a photon of energy when transferring from the lower to the higher spin state. The photon's energy is very small and occurs in the radio region of the spectrum. The precise energy difference depends on the chemical environment of the hydrogen atoms.

The position in the ¹H NMR spectrum where the absorption occurs for each hydrogen atom in the molecule is known as the chemical shift, and is measured in parts per million (ppm). The area under each peak corresponds to the number of hydrogen atoms in that particular environment.

A simplified correlation chart

Type of proton	Chemical shift / ppm
R — CH₃	0.9–1.0
— CH₂ — R	1.3–1.4
RO–C(=O)–CH₂—	2.0–2.5
R–C(=O)–CH₂—	2.2–2.7
R — O — H	1.0–6.0 (note the large range)
aromatic —H	6.9–9.0
R–C(=O)–H	9.4–10.0

¹H NMR spectrum of ethyl ethanoate $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3$

¹H NMR spectrum of ethanol CH_3CH_2OH

The additional trace integrates the area under each peak. The height of each section is proportional to the number of hydrogen atoms in each chemical environment.

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ⒽⓁ Nuclear magnetic resonance (NMR) spectroscopy

THE MAIN FEATURES OF ¹H NMR SPECTRA

1. **The number of different absorptions (peaks)**
   Each proton in a particular chemical environment absorbs at a particular frequency. The number of peaks thus gives information as to the number of different chemical environments occupied by the protons.

2. **The area under each peak**
   The area under each absorption peak is proportional to the number of hydrogen atoms in that particular chemical environment. Normally each area is integrated and the heights of the integrated traces can be used to obtain the ratio of the number of hydrogen atoms in each environment.

3. **The chemical shift**
   Because spinning electrons create their own magnetic field the surrounding electrons of neighbouring atoms can exert a shielding effect. The greater the shielding the lower the frequency for the resonance to occur. The 'chemical shift' (δ) of each absorption is measured in parts per million (ppm) relative to a standard. The normal standard is tetramethylsilane (TMS) which is assigned a value of 0 ppm. A table of chemical shifts is to be found in the IB data booklet.

4. **Splitting pattern**
   In ¹H NMR spectroscopy the chemical shift of protons within a molecule is slightly altered by protons bonded to adjacent carbon atoms. This spin–spin coupling shows up in high resolution ¹H NMR as splitting patterns. If the number of adjacent equivalent protons is equal to n then the peak will be split into (n + 1) peaks.

TMS AS THE REFERENCE STANDARD

$$CH_3$$

tetramethylsilane
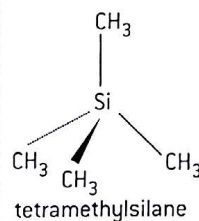
The advantages of using tetramethylsilane $Si(CH_3)_4$ as the standard reference are:

- All the protons are in the same environment so it gives a strong single peak.

- It is not toxic and is very unreactive (so does not interfere with the sample).

- It absorbs upfield well away from most other protons.

- It is volatile (has a low boiling point) so can easily be removed from the sample.

SPIN–SPIN COUPLING

Splitting patterns are due to spin–spin coupling. For example, if there is one proton (n = 1) adjacent to a methyl group then it will either line up with the magnetic field or against it. The effect will be that the methyl protons will thus experience one slightly stronger and one slightly weaker external magnetic field resulting in an equal splitting of the peak. This is known as a doublet (n + 1 = 2).

If there is a $-CH_2-$ group (n = 2) adjacent to a methyl group then there are three possible energy states available.

1. Both proton spins are aligned with the field
2. One is aligned with the field and one against it (2 possible combinations)
3. Both are aligned against the field.

This results in a triplet with peaks in the ratio of 1:2:1.

The pattern of splitting can always be predicted using Pascal's triangle to cover all the possible combinations.

This atom splits the methyl absorption into a doublet

These two H atoms split the methyl absorption into a triplet

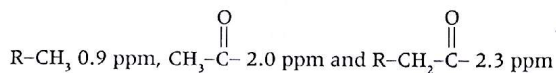| Number of adjacent protons (n)	Splitting pattern					Type of splitting
0			1			singlet
1		1		1		doublet
2		1	2	1		triplet
3	1	3	3	1		quartet
4	1	4	6	4	1	quintet

Thus a methyl group (n = 3) next to a proton will result in the absorption for that proton being split into a quartet with peaks in the ratio 1:3:3:1.

These three H atoms split the absorption due to the single proton into a quartet

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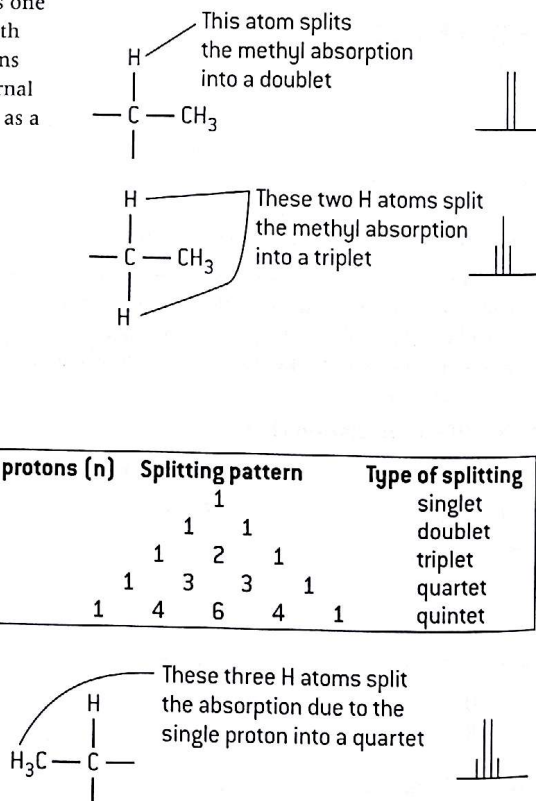
(HL) Applications of ^{1}H NMR spectroscopy

INTERPRETING A ^{1}H NMR SPECTRUM

1. The three different peaks show that the hydrogen atoms within the molecule are in three different chemical environments.

2. The integrated trace shows that the hydrogen atoms are in the ratio 2:3:3.

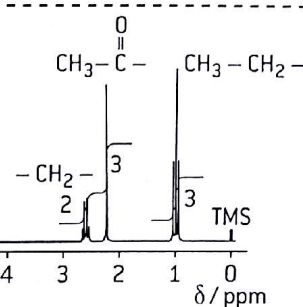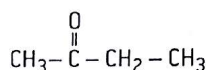3. The chemical shifts of the three peaks identify them as:

$$R-CH_3 \text{ 0.9 ppm}, \quad CH_3-\overset{\displaystyle O}{\overset{\|}{C}}- \text{ 2.0 ppm} \quad \text{and} \quad R-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}- \text{ 2.3 ppm}$$

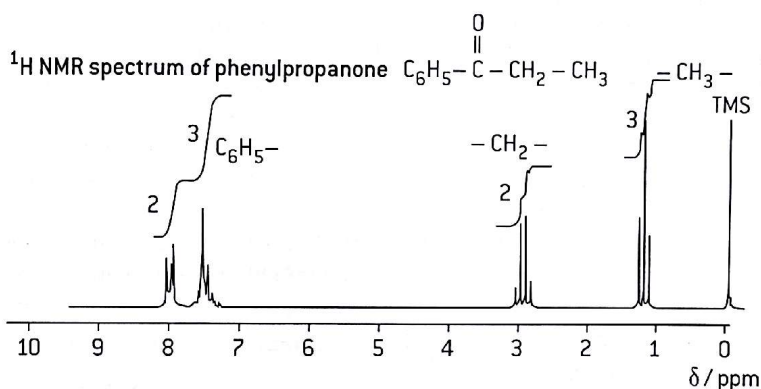4. The $-CH_2-$ group has three adjacent protons so is split into a quartet, $(n + 1 = 4)$.

The $CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-$ protons contain no adjacent protons so no splitting occurs.

The CH_3- group next to the $-CH_2-$ group is split into a triplet $(n + 1 = 3)$.

^{1}H NMR spectrum of butanone

$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-CH_3$$

$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-$ CH_3-CH_2-

$-CH_2-$ 3

2   3   TMS

10 9 8 7 6 5 4 3 2 1 0

δ / ppm

FURTHER EXAMPLES OF ^{1}H NMR SPECTRA INVOLVING SPLITTING PATTERNS

^{1}H NMR spectrum of phenylpropanone $C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-CH_3$

$-CH_3-$

3   C_6H_5- TMS

2   $-CH_2-$

2   3 $-CH_3-$

10 9 8 7 6 5 4 3 2 1 0

δ / ppm

^{1}H NMR spectrum of 1,1-dichloroethane $CHCl_2CH_3$

CH_3-

expansions

6.0 5.8 ppm   2.2 2.0 ppm

1 $-CHCl_2-$

3

TMS

10 9 8 7 6 5 4 3 2 1 0

δ / ppm
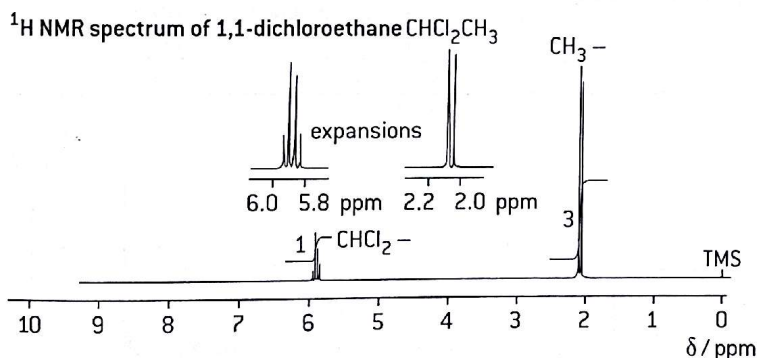
USES OF NMR SPECTROSCOPY

1. **Structural determination**
   ^{1}H NMR is a particularly powerful tool in structural determination as it enables information to be gained on the precise chemical environment of all the protons in the molecule. Similarly ^{13}C and other forms of NMR can also provide very detailed structural information including, for example, distinguishing between cis- and trans-isomers in organometallic compounds.

2. **Medicinal uses**
   NMR is particularly useful in medicine as the energy of the radio waves involved is completely harmless and there are no known side effects. ^{31}P is particularly useful in determining the extent of damage following a heart attack and in monitoring the control of diabetes. ^{1}H NMR is used in body scanning. The whole body of the patient can be placed inside the magnet of a large NMR machine. Protons in water, lipids and carbohydrates give different signals so that an image of the body can be obtained. This is known as MRI (magnetic resonance imaging). The image can be used to diagnose and monitor conditions, such as cancer, multiple sclerosis and hydrocephalus.

An MRI image of the human brain

(HL) Combination of different analytical techniques to determine structure

The determination of the organic structure of an unknown compound is usually achieved by combining the information from several different analytical techniques. This is illustrated by the following worked example for **Compound X**.
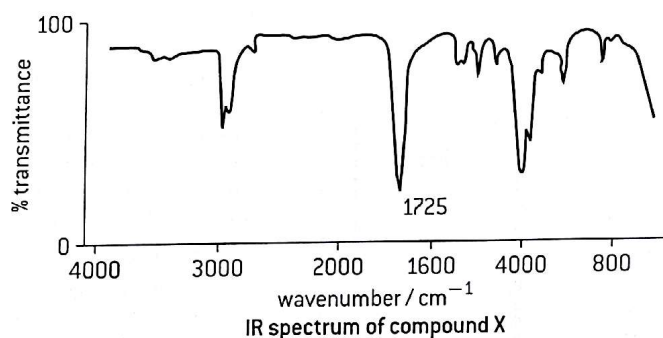
ELEMENTAL ANALYSIS

Compound X was found to contain 48.63% carbon, 8.18% hydrogen, and 43.19% oxygen by mass.

From this information the empirical formula of **Compound X** can be deduced as $C_3H_6O_2$.

Element	Amount/mol	Simplest ratio
C	48.63/12.01 = 4.05	3
H	8.18/1.01 = 8.10	6
O	43.19/16.00 = 2.70	2

INFRARED SPECTROSCOPY

IR spectrum of compound X

Information available from the infrared spectrum:

- Absorption at 2980 cm^{-1} due to presence of C–H in **Compound X**.
- Absorption at 1725 cm^{-1} due to presence of C=O in **Compound X**.
- Absorption at 1200 cm^{-1} due to presence of C–O in **Compound X**.
- Absence of broad absorption at 3300 cm^{-1} indicates **Compound X** does not contain O–H.

MASS SPECTROMETRY

Mass spectrum of compound X
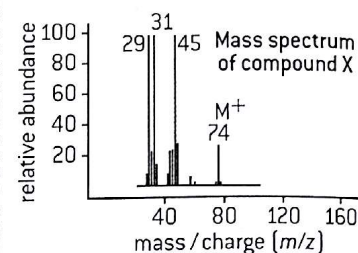
Information available from the mass spectrum:

- Since M$^+$ occurs at 74 the relative molecular mass of **Compound X** = 74.
- From this and the empirical formula it can be deduced that the molecular formula of **Compound X** is $C_3H_6O_2$.
- Fragment at 45 due to $(M - 29)^+$ so **Compound X** may contain C_2H_5– and/or CHO–.
- Fragment of 31 due to $(M - 43)^+$ so **Compound X** may contain C_2H_5O–
- Fragment at 29 due to $(M - 45)^+$ so **Compound X** may contain

$$HOOC-\text{ or } H-\overset{\overset{\displaystyle O}{\|}}{C}-O-.$$
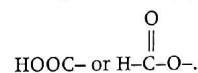
- Peak at 75 due to the presence of ^{13}C.

¹H NMR SPECTROSCOPY

Information available from the ¹H NMR spectrum:

- Number of separate peaks is three so **Compound X** contains hydrogen atoms in three different chemical environments.
- From the integration trace the hydrogen atoms are in the ratio of 3:2:1 for the peaks at 1.3, 4.2 and 8.1 ppm respectively. Since there are six hydrogen atoms in the molecule this is the actual number of protons in each environment.

¹H NMR spectrum of compound X
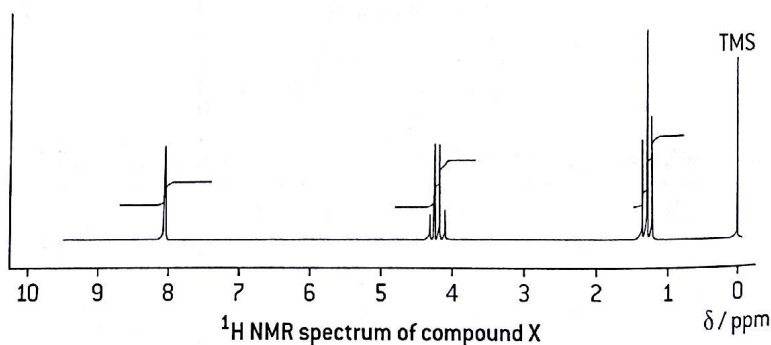
- From the IB data booklet the chemical shift may be attributed to following types of proton.

1.3 ppm   R–CH$_3$ (cannot be R–CH$_2$–R as it is for three protons)

4.2 ppm $R-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-R$

8.1 ppm   not in IB data booklet but consistent with $H-\overset{\overset{\displaystyle O}{\|}}{C}-O-R$.

- From the splitting patterns the number of adjacent hydrogen atoms can be determined.
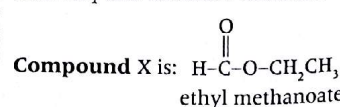
1.3 ppm	triplet	two adjacent hydrogen atoms
4.2 ppm	quartet	three adjacent hydrogen atoms
8.1 ppm	singlet	no adjacent hydrogen atoms

IDENTIFICATION

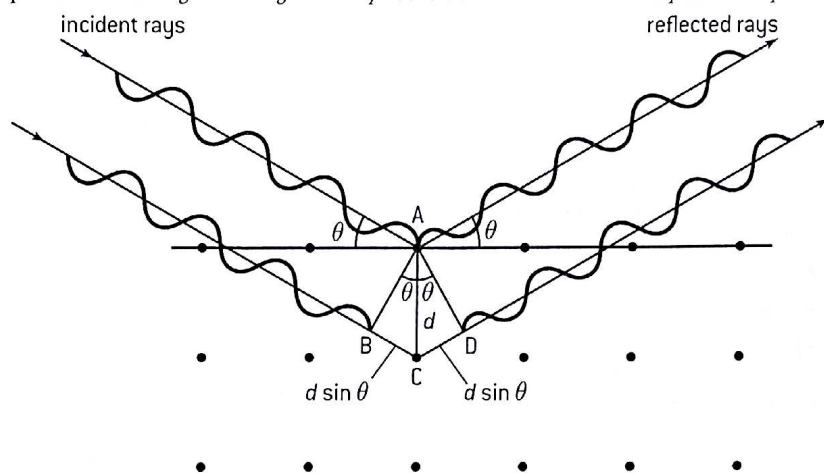All the above information is consistent with only one definitive structure:

Compound X is: $H-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2CH_3$
ethyl methanoate

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HL X-ray crystallography

## MULTIPLE CHOICE QUESTIONS – MEASUREMENT, DATA PROCESSING AND ANALYSIS

1. A 25.0 cm³ sample of a base solution of unknown concentration is to be titrated with a solution of acid of unknown concentration. Which of the following technique errors would give a value for the concentration of the base that is **too high**?

   I. The pipette that is used to deliver the base solution is rinsed only with distilled water before delivering the sample to be titrated.

   II. The burette that is used to measure the acid solution is rinsed with distilled water but not with the solution of the titration.

   A. I only
   B. II only
   C. Both I and II
   D. Neither I nor II

2. In a school laboratory, which of the items listed below has the greatest relative uncertainty in a measurement?

   A. A 50 cm³ burette when used to measure 25 cm³ of water
   B. A 25 cm³ pipette when used to measure 25 cm³ of water
   C. A 50 cm³ graduated cylinder when used to measure 25 cm³ of water
   D. An analytical balance when used to weigh 25 g of water

3. A piece of metallic indium with a mass of 15.456 g was placed in 49.7 cm³ of ethanol in a graduated cylinder. The ethanol level was observed to rise to 51.8 cm³. From these data, the best value one can report for the density of indium is

   A. 7.360 g cm⁻³
   B. 7.4 g cm⁻³
   C. 1.359×10^{-1} g cm⁻³
   D. 32.4 g cm⁻³

4. A mixture of sodium chloride and potassium chloride is prepared by mixing 7.35 g of sodium chloride with 6.75 g of potassium chloride. The total mass of the salt mixture should be reported to _____ significant figures; the mass ratio of sodium chloride to potassium chloride should be reported to _____ significant figures, and the difference in mass between sodium chloride and potassium chloride should be reported to _____ significant figures. The numbers required to fill the blanks above are, respectively,

   A. 4, 3, 2
   B. 4, 2, 2
   C. 3, 3, 1
   D. 4, 3, 1

5. Repeated measurements of a quantity can reduce the effects of

   A. both random and systematic errors
   B. neither random nor systematic errors
   C. only systematic errors
   D. only random errors

6. A 50.0 cm³ pipette with an uncertainty of 0.1 cm³ is used to measure 50.0 cm³ of 1.00 ± 0.01 mol dm⁻³ sodium hydroxide solution. The amount in moles of sodium hydroxide present in the measured volume is

   A. 0.0500 ± 0.0010
   B. 0.0500 ± 0.0001
   C. 0.0500 ± 0.0012
   D. 0.0500 ± 0.0006

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7. Consider the following three sets each of five measurements of the same quantity which has an accurate value of 20.0.

I.	II.	III.
19.8	19.2	20.0
17.2	19.1	19.9
18.3	19.3	20.0
20.1	19.2	20.1
18.4	19.2	20.0

Which results can be described as precise?

A. I, II and III   C. II and III

B. II only   D. III only

8. A thermometer with an accuracy of ± 0.2 °C was used to record an initial temperature of 20.2 °C and a final temperature of 29.8 °C. The temperature rise was

A. 9.6 ± 0.4 °C   C. 10 °C

B. 9.6 ± 0.2 °C   D. 9.6 ± 0.1 °C

9. An experiment to determine the molar mass of solid hydrated copper(II) sulfate, $CuSO_4.5H_2O$ gave a result of 240 g. The experimental error was

A. 0.04%   C. 10%

B. 4%   D. 50%

10. Which sketch graph shows interpolation to find an unknown value.

A.   B.   C.   D.
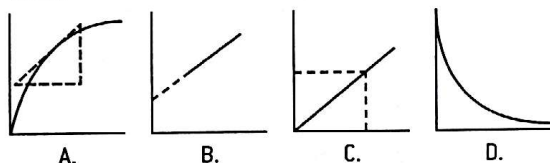
11. What information can be obtained from the number of peaks in the ^1H NMR spectrum of a compound?

A. The number of different chemical environments occupied by the protons in one molecule of the compound.

B. The number of hydrogen atoms in one molecule of the compound.

C. The number of different functional groups in one molecule of the compound.

D. The number of carbon atoms in one molecule of the compound.

12. What is the index of hydrogen deficiency (IHD) for a compound with the molecular formula C_7H_8?

A. 3   C. 6

B. 4   D. 8

13. The mass spectrum of a compound shows peaks with m/z values of 88, 73, 59 and 43. Which compound could give this spectrum?

A. $HCOCH_2CH_2CH_3$ C. $CH(CH_3)_2COOH$

B. $CH_3CH_2COOCH_2CH_3$ D. $CH_3CH_2CH_2COOH$

14. Which is correct about the regions of the electromagnetic spectrum?

	Region of spectrum	Energy	Wavelength
A.	Ultraviolet	Highest	Longest
B.	Infrared	Highest	Shortest
C.	Radio	Lowest	Longest
D.	Visible	Lowest	Shortest

HL

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15. The ^1H NMR spectrum of a particular compound shows three separate peaks. The relative height of each integration trace and the splitting patterns are

Peak number	Integration trace	Splitting pattern
1	3	triplet
2	2	quartet
3	1	singlet

Which compound could give this spectrum?

A. $HCOOCH_2CH_3$ C. $CH_3CH_2COOCH_3$

B. $CH_3CH_2CH_2COOH$ D. $CH_3CH(OH)CH_3$

16. Which are advantages for using tetramethylsilane as a standard reference in ^1H NMR?

I. All its protons are in the same chemical environment.

II. It is chemically unreactive.

III. It does not absorb energy in the same region as most other protons.

A. I and II only   C. II and III only

B. I and III only   D. I, II and III

17. Which compound will contain a peak with a triplet splitting pattern in its ^1H NMR spectrum?

A. CH_3OH C. $CH_3CHClCOOH$

B. CH_3CH_2COOH D. $(CH_3)_3COH$

18. Which can be determined by single crystal X-ray crystallography?

I. Bond lengths

II. Bond angles

III. Chemical structure

A. I and II only   C. II and III only

B. I and III only   D. I, II and III

SHORT ANSWER QUESTIONS – MEASUREMENT, DATA PROCESSING AND ANALYSIS

1. A simulated computer-based experiment was performed to determine the volume of nitrogen generated in an airbag from the decomposition of sodium azide, NaN_3.

$$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$$
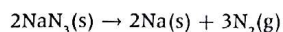
The following data were entered into the computer.

Mass of $NaN_3(s)$/ kg(± 0.001 kg)	Temperature / °C (± 0.50 °C)	Pressure / kPa ± 1 kPa
0.072	20.00	106

a) State the number of significant figures for the mass, temperature and pressure data. [1]

b) Calculate the amount (in mol) of sodium azide present. [2]

c) Calculate the percentage uncertainty for each of the mass, temperature and pressure. [1]

d) Determine the volume of nitrogen gas (in dm³) produced under these conditions together with its uncertainty assuming complete decomposition of the sodium azide. [5]

2. a) Elemental analysis of Compound **X** shows that it contains 15.40% carbon, 3.24% hydrogen and 81.36% iodine by mass. Determine the empirical formula of Compound **X**. [1]

b) The mass spectrum of Compound **X** is shown below.
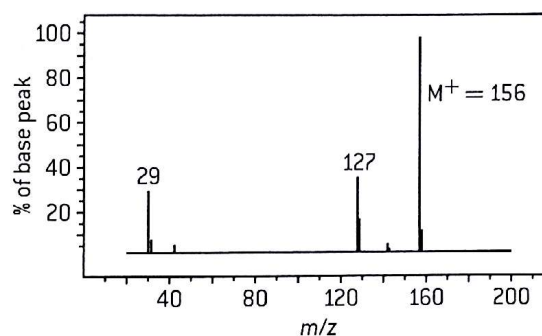
(i) Deduce the molecular formula of Compound **X**. [1]

(ii) Calculate the index of hydrogen deficiency (IHD) for Compound **X**. [1]

(iii) Identify the fragments responsible for the peaks with *m/z* values of 127 and 29. [2]

(iv) Deduce the identity of Compound **X**. [1]

c) The ¹H NMR spectrum for Compound **X** shows two peaks with integration traces of two units and three units respectively. Explain how this information is consistent with your answer to (b) (iv). [2]

3. ¹H NMR spectroscopy can be used to distinguish between pentan-2-one and pentan-3-one. In each case state the number of peaks in their ¹H NMR spectra and state the ratios of the areas under each peak. [4]

HL

4. The ¹H NMR spectra of an unknown compound is given below:
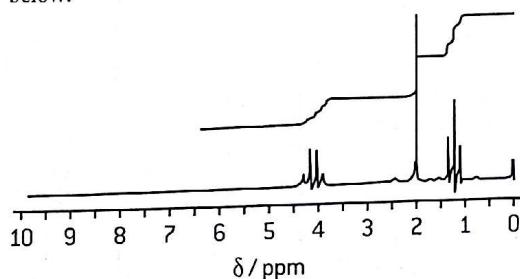
a) Why is tetramethylsilane used in ¹H NMR spectroscopy? [1]

b) What word is used to describe the multiplicity of the peaks centred at 4.1 ppm? [1]

c) What is the ratio of the number of hydrogen atoms responsible for the chemical shifts centred at 1.2, 2.0 and 4.1 ppm respectively? [1]

d) Two structures that have chemical shifts centred at 4.1 ppm are $RCOOCH_2R$ and $C_6H_5OCOCH_3$. From consideration of the rest of the spectra only one of these general structures is possible. Identify which one and explain your reasoning. [2]

Below is the infrared spectrum of the same compound:
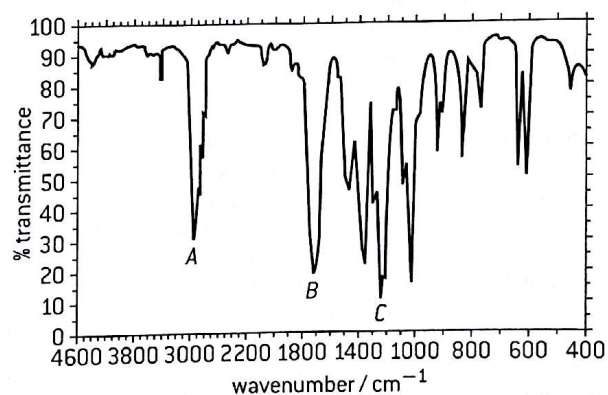
e) Identify which particular vibrations are responsible for the peaks labelled *A*, *B* and *C*. [3]

f) The mass specturm of the same compund shows a molecular ion peak at 88 *m/z*. The fragmentation pattern shows prominent peaks at 73 *m/z* and 59 *m/z* amongst others. Identify the ions responsible for these peaks. [3]

g) Give the name and structural formula of the compound. [2]

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