Chemistry Option A: Modern Analytical Chemistry Notes

(HL & SL)

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Compiled from the IB Chemistry Guide for examinations beginning 2009, IB Past Papers, and Richard

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Chapter A: Modern Analytical Chemistry

Analytical techniques
A.1.1 State the reasons for using analytical techniques.(2m)
- Structure determination
- Analysis of composition of substances
- To determine purity

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.
- information from only one technique is usually insufficient to determine or confirm a structure.

Principles of spectroscopy
A.2.1 Describe the electromagnetic spectrum. (NA)
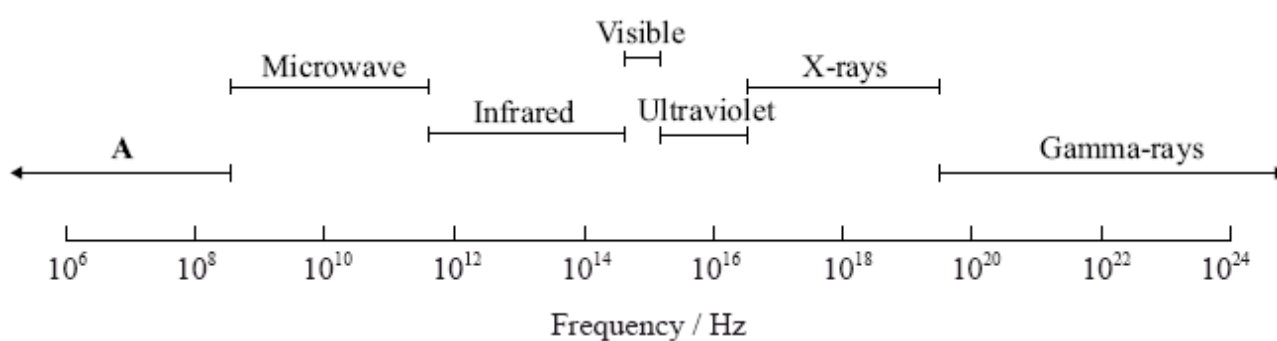
- Comprises of all the different wavelengths of electromagnetic radiation.
- Wave number = 1/wavelength in cm
- Speed of light = wavelength x frequency
- Energy = Planck's constant x frequency

A.2.2 Distinguish between *absorption* and *emission* spectra and how each is produced. (2m)

- absorption spectrum: energy required to move/excite (electrons) from <u>lower/ground</u> state to higher energy level/excited state;

- emission spectrum: radiation emitted by electrons from <u>higher/excited</u> state to lower/ground energy level;

    OR

- absorption spectrum: continuous spectrum with missing regions/lines corresponding to energies absorbed;

- emission spectrum: regions/lines corresponding to energies given out/emitted;

A.2.3 Describe the atomic and molecular processes in which absorption of energy takes place. (3m)

- Rotation -microwave
- Vibration , stretches, bending - IR
- Electronic transition -UV

Infrared spectroscopy

A.3.1 Describe the operating principles of a double-beam IR spectrometer. (3-4m)
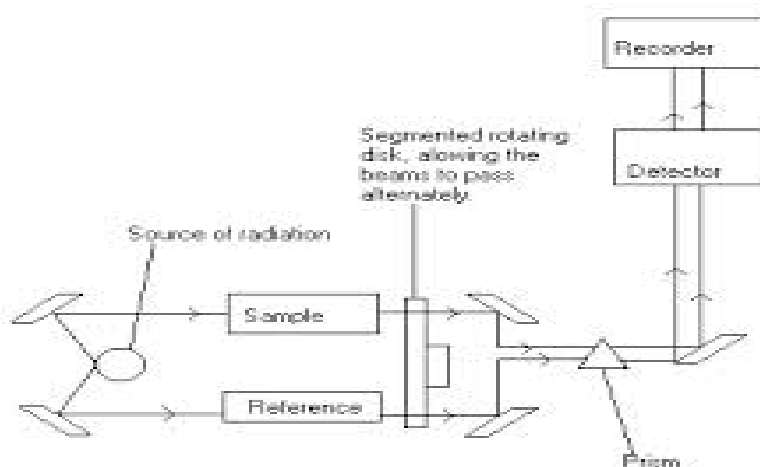
- monochromator (to create single wavelength);

- (rotating) mirrors/beam splitting;

- sample and reference (to compare);

- photomultiplier detector;

A.3.2 Describe how information from an IR spectrum can be used to identify bonds.

A.3.3 Explain what occurs at a molecular level during the absorption of IR radiation by molecules. (3m)

- Change in dipole movement leads to IR absorption;
- Symmetric stretching is IR inactive;
- Asymmetric stretching and symmetric bending are IR active as it induces dipole movement;

Eg: H2O, –CH2–, SO2 and CO2

If a molecule has a moving dipole when it vibrates then it will be IR active. For bent molecules (water, sulphur dioxide, -CH2-) there are 3 vibration modes you need to know and ALL of them are IR active since the dipole moves during vibration. Modes are:
Asymmetrical stretching (imagine punching your own chin with alternate fists)
Symmetrical stretching (punch your chin with both fists at the same time)
Bending (bang your knuckles together beneath your chin)

For many linear molecules (eg CO2) one mode is IR INACTIVE (the IB love this) -- the vibration does not move the dipole = symmetrical stretching.
Asymmetrical stretching (imagine slapping your own ears left, right,left, right with both hands)
Symmetrical stretching (slap your ears together)
Bending (down stroke your ears)

Eg1: Identify which of the following molecules absorbs IR radiation and explain your choice.

$$H_2 \quad O_2 \quad HCl$$

- HCl;

- vibration/stretching of bond/molecule produces a <u>change</u> in **dipole moment/polarity**;

Eg2: Explain what occurs at a molecular level during the absorption of infrared (IR) radiation by the sulfur dioxide molecule, SO_2.
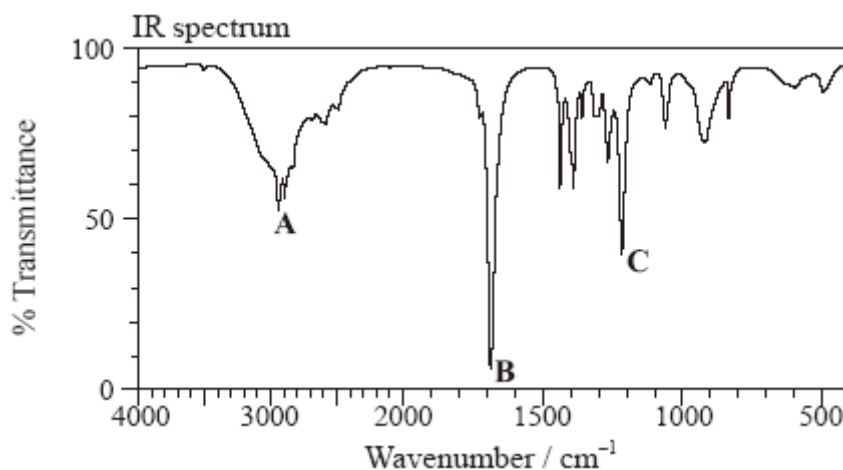
- (O–S–O) bond angle changes;

- (S–O) bond (length) stretches;

    Allow [1] for S–O bond vibrations if neither of the above points are scored.

- polarity of SO_2 molecule changes;

A.3.4 Analyse IR spectra of organic compounds.

The IR spectrum of an unknown compound, **X**, of molecular formula $C_3H_6O_2$ is as follows.

[Source: SDBSWeb: http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology)]

(i)   Identify the bonds responsible for the peaks **A**, **B** and **C** in the IR spectrum of **X**.

A: O–H
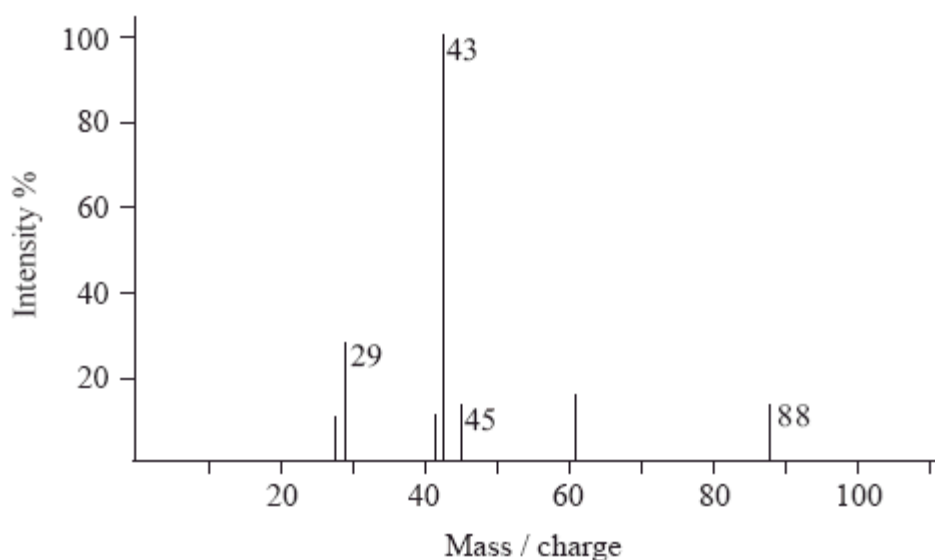**B**: C=O
C: C–O

(2)

Refer to table 17 in Data Booklet

Mass Spectroscopy

A.4.1 Determine the molecular mass of a compound from the molecular ion peak.

Eg: The mass spectrum of an unknown compound, **X**, of empirical formula C_2H_4O is shown below.

[Source: Cleapss Guides: L202 Spectra (Cleapss School Science Service), Sept 2000.]

    (i)   Determine the relative molecular mass of **X** from the mass spectrum and deduce the formula of the molecular ion.

- 88;
  Do not award mark if units are given.

- $C_4H_8O_2^+$;

A.4.2 Analyse fragmentation patterns in a mass spectrum to find the structure of a compound.
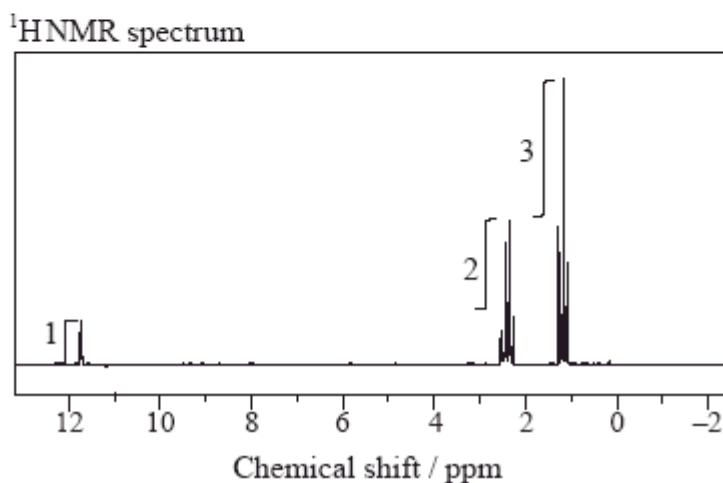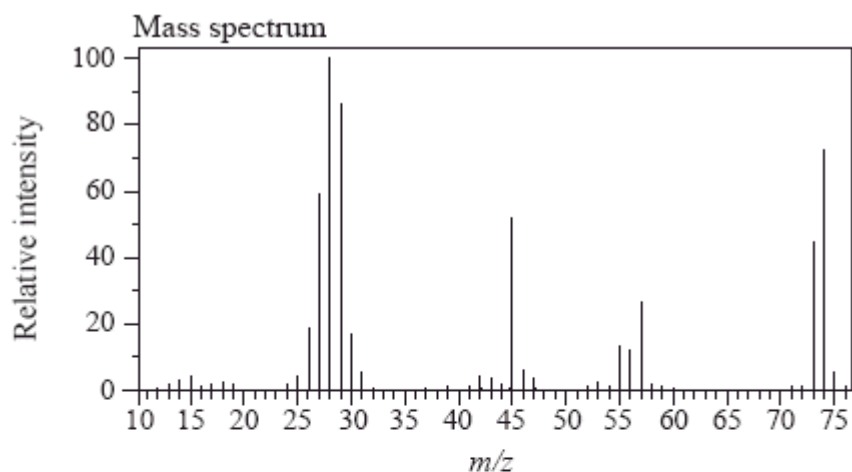Examples of fragments should include:
- $(Mr - 15)+$ loss of CH3
- $(Mr - 17)+$ loss of OH
- $(Mr - 29)+$ loss of C2H5 or CHO
- $(Mr - 31)+$ loss of CH3O
- $(Mr - 45)+$ loss of COOH.

# Nuclear Magnetic Resonance (NMR) Spectroscopy

A.5.1 Deduce the structure of a compound given information from its 1H NMR spectrum.

Eg: The mass spectrum and ^{1}H NMR spectrum of an unknown compound, **X**, of molecular formula $C_3H_6O_2$ are as follows.

[Source: SDBSWeb: http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology)]

(ii) In the mass spectrum of **X**, deduce which ions the m/z values at 74, 45 and 29 correspond to.

$m/z = 74$: $C_2H_5COOH^+$ / $C_3H_6O_2^+$;

$m/z = 45$: $COOH^+$;

$m/z = 29$: $C_2H_5^+$;
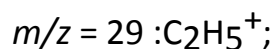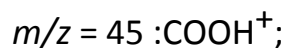
Penalize missing + charge once only.

        (iii)   Identify the peak at 11.73 ppm in the ^{1}H NMR spectrum.

. −COOH;

(1)

        (iv) Deduce the structure of **X**.

CH$_3$CH$_2$COOH / CH$_3$CH$_2$CO$_2$H;

Eg: Distinguish between the ^{1}H NMR spectra of 1-bromopropane and 2-bromopropane (splitting patterns are not required).

- 2-bromopropane will show two separate absorptions/peaks;
- in the ratio 6:1;
- 1-bromopropane will show three separate absorptions/peaks;
- in the ratio 3:2:2;

Eg: (i) The ^{1}H NMR spectrum of **X,** molecular formula $C_4H_8O_2$, shows three peaks. State the information that can be obtained from the number of peaks.

- the number of different hydrogen/proton environments

(1)

(ii) The ^{1}H NMR spectrum of **X** includes peaks at 2.0 and 4.1 ppm. Use Table 18 of the Data Booklet to suggest the chemical shift of the third peak and state its relative peak area. Show your answers in the table below.

Peak	Chemical shift / ppm	Relative peak area
First	2.0	3
Second	4.1	2
Third	0.9-1.0	3

(2)

(iii) Deduce a possible structure for **X** that is consistent with the mass, IR and ^{1}H NMR spectra.

$/ CH_3CO_2CH_2CH_3$;
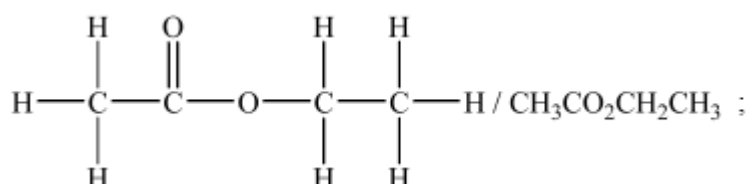
A.5.2 Outline how NMR is used in body scanners (3m)

- human body consists of 70 %/mostly/a lot of water;

- protons in water molecules/in carbohydrates, proteins and fats can be detected by MRI;

- organs have different water to lipid ratios;

- water in different environments;

- so that protons have different environments so produce different effects;

- a 3D image is obtainable

A.9.1 Explain the use of tetramethylsilane (TMS) as the reference standard. (1m)

1) The silicon in the molecule moves the peak away from those in your sample (which is unlikely to contain Si)
2) Unreactive (strong bonds in the molecule require lots of energy to break)
3) Low boiling point (low surface area and a non polar molecule)
4) 1 peak on NMR (only one hydrogen environment)
5) Soluble in most organic solvents (which normally have non-polar characteristics)

A.9.2 Analyse 1H NMR spectra.

- The number of peaks = the number of different hydrogen environments in the molecule.
- Area under the peaks = ratio of H atoms in each environment.
- Chemical shifts = the environment of H
- Splitting patterns (singlets, doublets, triplets and quartets.) = Number of H to adjacent C.

* Spin-spin coupling between adjacent protons cause the peaks to split in to n+1 peaks
* H interchangeable with proton

Eg: Distinguish between the ^{1}H NMR spectra of 1-bromopropane and 2-bromopropane (splitting patterns are not required).

- 2-bromopropane will show two separate absorptions/peaks;

- in the ratio 6:1;

- 1-bromopropane will show three separate absorptions/peaks;

- in the ratio 3:2:2;

Eg: A feature of some ^{1}H NMR spectra is the electron-withdrawing effect of electronegative atoms. These atoms cause nearby protons to produce peaks at higher chemical shift values, often in the range 2.5 to 4.5 ppm.

Consider the ^{1}H NMR spectrum of an unknown compound, D, which has a molecular formula $C_4H_8O_2$ and is known to have an absorption in its IR spectrum corresponding to a C=O absorption.

Chemical shift / ppm
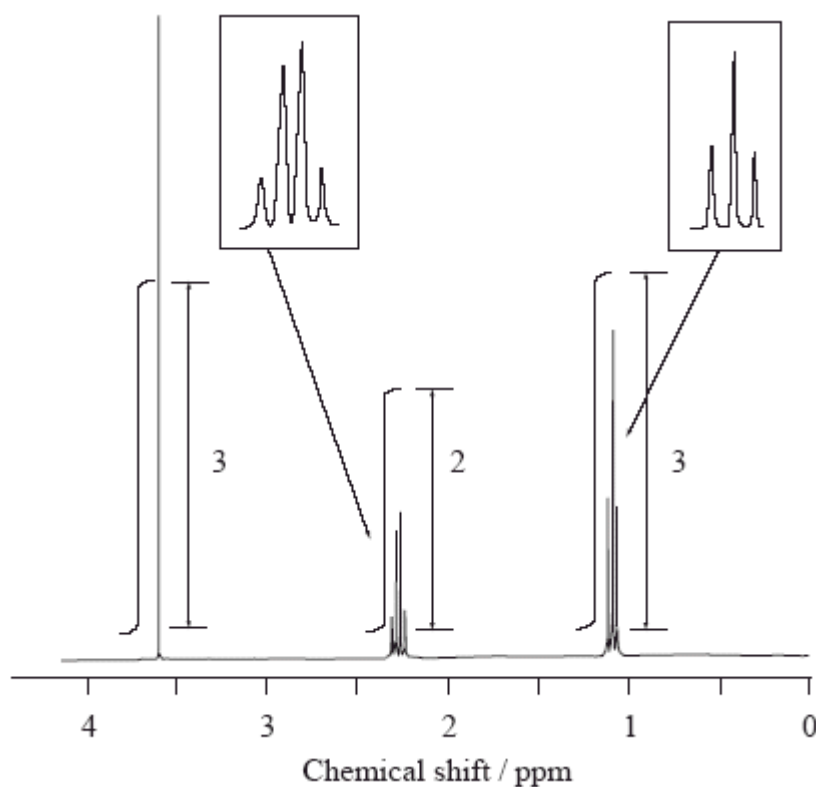
Use this information and the values in Table 18 of the Data Booklet to deduce the structure of D.

- D could be $CH_3CH_2COOCH_3$ or $CH_3COOCH_2CH_3$;

- this is because there are 3 peaks / 3:2:3 ratio;

- explanation of splitting into a singlet, a triplet and a quartet;

- methyl propanoate/$CH_3CH_2COOCH_3$ is correct isomer because of higher chemical shift value of singlet (3.6 instead of 2.0–2.5);

(4Max)

Atomic absorption spectroscopy

A.6.1 State the uses of AA spectroscopy. (1m)
- Identification/detection/concentration of metals/ metal ions in water (Cu), blood (Ca/Mg/Al/Cu/Na/K) , soils (Al/Fe), paint (Pb), foods

A.6.2 Describe the principles of atomic absorption. (4m)

- make up different solutions of known concentrations;

- measure the absorbance for each concentration;

- plot a calibration/absorbance against concentration curve;

- read the value of unknown concentration from its absorbance

- compare the absorption of the unknown with the standard solutions

A.6.3 Describe the use of each of the following components of the AA spectrophotometer: fuel, atomizer, monochromatic light source, monochromatic detector and readout.

- Fuel- to produce heat
- Atomiser- converts ions in a sample into atoms
- Monochromatic light source- produces light of same frequency as is absorbed by the species (being detected)
- Monochromatic detector – detects light of the same frequency/ converts photons into electric signal

A.6.4 Determine the concentration of a solution from a calibration curve.

Eg: A calibration curve was plotted using water with known concentrations of lead ions.
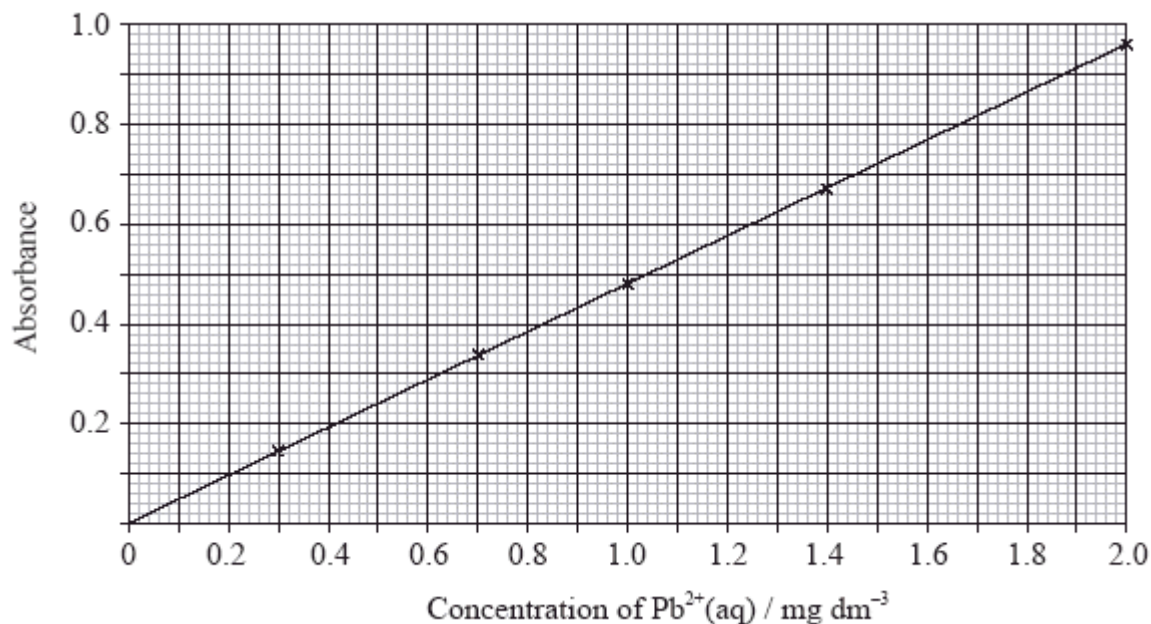
100 dm^3 of the contaminated drinking water was reduced by boiling, to 7.50 dm^3. It was found that when the reduced volume was tested it had an absorbance of 0.55.

Calculate the concentration of lead ions (in mg dm^{-3}) in the original contaminated drinking water.

- concentration of Pb^{2+} from graph = 1.15 (mg dm^{-3});

  Allow between 1.13 and 1.17 mg dm^{-3}.

- original concentration = 1.15 × $\dfrac{7.5}{100}$

$$= 8.63 \times 10^{-2} \text{ (mg dm}^{-3});$$

Chromatography

A.7.1 State the reasons for using chromatography. (2m)

- Qualitative and quantitative analysis
- Separation of mixture into individual components
- Identification of constituents of mixture
- Determine mass

A.7.2 Explain that all chromatographic techniques involve adsorption on a stationary phase and partition between a stationary phase and a mobile phase. (4m)

- Stationary phase – adsorption
- Mobile phase - partition
- The mixture of chemicals PARTITION by being differently DISSOLVED in the MOBILE PHASE and ADSORBED onto the STATIONARY PHASE
- distance travelled/separation (of components) depends on adsorption between two phases

A.7.3 Outline the use of paper chromatography, thin-layer chromatography (TLC) and column chromatography. (4-6m)

- Paper Chromatography uses cellulose as the stationary phase. Mixtures of inks or even sugars will partition between the stationary phase and the mobile phase (eluent). Mobile phases can be water, alcohol, propanone etc.
- TLC is used to separate biological mixtures (eg amino acids). The stationary phase here is alumina or silica.
- Developers, such as ninhydrin may be needed to see invisible components.
- Column chromatography uses a tube plugged with glass wool and filled with alumina or silica. This is used for bulk separations. Solvents can be changed during the experiment. Different substances can then be individually collected.

- R_f value is the ratio between the distance moved by the spot and the distance moved by the solvent front

- Unknown substance can be identified by comparing R_f value of unknown against known values under the same conditions

A.10.1 Describe the techniques of gas–liquid chromatography (GLC) and high performance liquid chromatography (HPLC). (4-6m)

GLC
- Sample vapourised/ heated;
- Assumes sample does not decompose at high temperature;
- Different components carried through apparatus in stream of carrier gas;
- Mobile phase inert/nitrogen/helium/argon;
- Stationary phase liquid/long chain alkane/hydrocarbon/grease adsorbed on solid support;
- Each component has a different attraction the hydrocarbon/ attraction of components depends on molecular mass and polarity;
- Less volatile components have longer retention time/ components pass through at different rates;
- Components detected by flame ioniser;
- Converted to electrical current/ connected to mass spectrometer;

(5Max)

HPLC
- (non-polar or polar) mobile/liquid phase **and** (short, polar or non-polar) solid/stationary phase;
- Mobile phase forced (through the column) under pressure (at constant temperature);
- Sample placed in liquid stream/components separate as they pass through tube;
- Detected by absorption of UV/fluorescence/conductivity;

- Components reach detector at different times/R_t/ compare retention times to standard samples (under identical conditions);

(4Max)

Chromatographic technique	Stationary phase	Mobile phase
HPLC	Silica/silicon (di)oxide/SiO_2 and/or long chain hydrocarbon (on column);	hexane / water / alcohol / solvent / liquid;
GLC	Alkane / long chain hydrocarbon (on column);	N_2(g) / He(g) / Ar(g);

- GLC Is suitable for the determination of blood alcohol levels but not for the separation of sugar samples because:
- GLC involves vaporising a sample at high temperature;
- Alcohols can (easily) vaporise without decomposing/ sugar molecules are temperature sensitive/decompose at high temperature

*HPLC can identify compounds that are temperature-sensitive. (cool)
eg analysis of oil; alcoholic beverages; antioxidants, sugars and vitamins in foods; pharmaceuticals; polymers; biochemical and biotechnology research; quality control of insecticides and herbicides.

*GLC can identify compounds that can vaporize (using the inbuilt oven) without decomposing. (hot)
Uses include: analysis of urine samples from athletes for drugs, underground mine gases and blood alcohol levels.

Visible and ultraviolet spectroscopy
A.8.1 Describe the effect of different ligands on the splitting of the d orbitals in transition metal complexes. (3-4m)

Explanation of colour change

- d orbitals splits (into two levels);

- due to repulsion between d electrons and non-bonding electrons on ligand

- Electrons on lower energy level absorb radiation from visible spectrum
- Absorption depends on energy difference between the split d orbitals;

- (visible light absorbed as) electrons move from lower to higher energy d orbitals;

- colour observed complementary to absorbed;

Explanation of why changing ligands changes colour

- colour observed depends energy difference between split levels.

- more electron-dense ligand greater splitting of d orbitals;

- NH_3 ligand has greater (crystal field/ligand) splitting energy

- Absorption moves towards blue end of spectrum

A.8.2 Describe the factors that affect the colour of transition metal complexes. (2m)

- Identity of metal ion - Different metals have *different d-orbital splitting* due to different *numbers of protons* in the nucleus

- Oxidation number of metal - affects the *size of the d orbital* splitting due to the different *number of electrons present*
- Identity of ligand –different ligands *have different electron densities* causing *different amounts of splitting of d orbital*, so absorbing radiation from different part of the spectrum.

A.8.3 State that organic molecules containing a double bond absorb UV radiation.

A.8.4 Describe the effect of the conjugation of double bonds in organic molecules on the wavelength of the absorbed light. (2m)

- Greater conjugation of double bonds increases the delocalisation
- less energy required to excite delocalised electrons
- higher wavelength/ lower frequency, absorbed in the visible range (not UV), so it appears coloured

A.8.5 Predict whether or not a particular molecule will absorb UV or visible radiation. (2m)

- retinol (absorbs visible light as it) contains conjugated double bonds/delocalized electrons;

- less energy is required (to excite the electrons);

- absorption occurs in the visible region

- cholesterol absorbs in the UV region as it contains one double C=C bond / does not absorb in the visible region as it has no conjugated double bonds;

A.8.6 Determine the concentration of a solution from a calibration curve using the Beer–Lambert law. (4m)

1) Find the most absorbed wavelength in your sample using a spectrometer.
2) Accurately measure the colour of multiple concentrations of your sample.
3) Plot a graph of concentration against concentration -- tah dah you have a calibration curve based on the Beer-Lambert Law. Now you can find the unknown concentrations of other samples.

*Absorbance = log Io/ I = elc where
Io= intensity of incoming light
I=intensity of outgoing light e= constant for the substance
l =path length of light through the substance c=concentration of substance