Modern Analytical Chemistry

OPTION A

A1 Analytical Techniques (SL/HL)

- Analytical techniques are an important and useful tool for the following reasons:

a) They allow the exact composition of substances/compounds/elements to be determined.

b) The formula of the compounds can be derived.

c) They allow a detailed structure to be deduced.

d) They are able to determine the purity of the substances investigated.

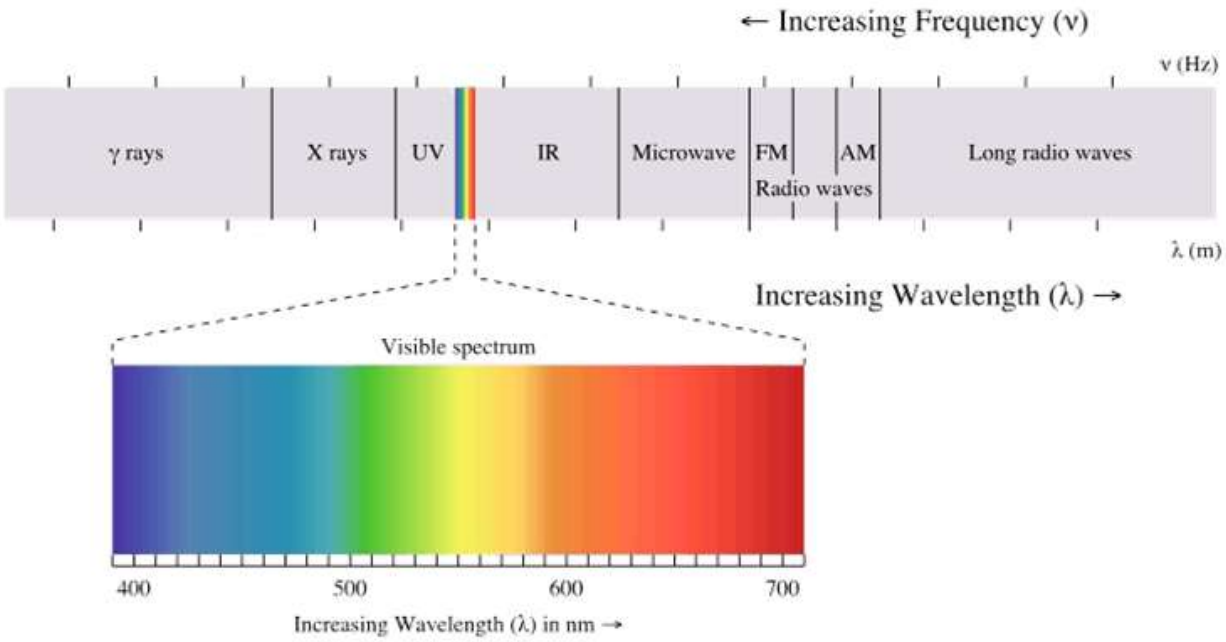
- The **composition** of substances can be determined by separation techniques such as **chromatography**. (Paper, thin layer, column (SL/HL), gas-liquid, high performance liquid (HL).
- The **concentration** of substances can be deduced by process such as atomic absorption (AA) spectroscopy (SL/HL), UV and visible spectroscopy (HL).
- The **formula** of a compound can be determined from a variety of techniques.
    1. **Chemical tests** will determine the functional groups present.
    2. **Empirical formula** can be worked out by combustion with oxygen and then determining the mass of CO_2 and H_2O given.
- The **structure** of a compound requires a **combination** of modern instrumental methods.
    1. **Mass Spectrometry.**
    2. **Infra Red Spectroscopy.** (I.R.)
    3. **Nuclear Magnetic Resonance** (NMR)

A2 Principles of Spectroscopy (SL/HL)

Electromagnetic Spectrum

- Radiation is related by the equation c= λf. The greater the energy, the higher the frequency, the lower the wavelength.

Label the main regions of the spectrum and the wavelengths/frequencies.



TOK: How is the electromagnetic spectrum used to transfer information? Discuss how using this energy has affected our lives. What are the limits to its usefulness, if any?

Absorption and Emission Spectra

- Emission Spectroscopy involves analysis of light given out by atoms/molecules as they return to their ground state.

- Absorption Spectroscopy involves energy being absorbed by the atoms/molecules to promote into excited states.

- The energy absorbed/emitted is characteristic to the atom/molecule involved.

- The most energetic absorptions involve electron transitions. These take place in the X-ray, γ-ray, UV and visible regions, depending on which electrons move.

- Molecular vibrations (stretching and bending) cause less energetic absorptions. These occur in the IR region.

- Molecular rotations occur in the microwave region. The weakest transitions involve nuclear spin. These occur in the radio wave region (see nmr).

- Label the electromagnetic spectrum above with the types of transition that causes absorption.

A3 Infra Red Spectroscopy (SL/HL)

- Used to determine which **bonds** are present in the molecule.

- If an unknown organic molecule is subjected to I.R. energy, its bonds will **absorb** some of the radiation causing them to bend, stretch and vibrate.

- Different bonds will absorb the radiation at **different wavelengths** of radiation allowing them to be identified.

- Absorptions are measured as **wavenumbers (1/wavelength)**

- Weaker bonds require less energy and so absorption occurs at a lower wavenumber.

Operating Principles

- An infrared source produces radiation of the required frequency range.

- A rotating mirror alternately passes the radiation through the sample and then through a reference.

- A photomultiplier then converts these photons of light into an electrical current.

- The spectrum is generated by a comparison between the sample and reference beams. This is called a **double beam spectrometer**.

Draw and label a simple diagram:

Types of Vibration

- Only vibrations that involve a **change in polarity** will absorb infrared radiation.
- Molecules that are perfectly **non-polar** (O_2, H_2 etc.) Will not therefore give absorptions.
- With non-polar molecules that contain polar bonds (CO_2, CCl_4) the type of vibration is important.
- **Symmetrical stretching** would not cause absorption since the dipoles would cancel. **Asymmetrical stretching** would cause absorption, as would any type of **bending** of the bonds.

E.g. CO_2 symmetrical stretch asymmetrical stretch bending

E.g. SO_2

E.g. H_2O

Extension: Draw out some of the possible bending and stretching vibrations in $–CH_2-$

Note: There are lots of types of bending vibrations such as scissoring, rocking, twisting and wagging.

Analysing IR Spectra

Mainly used to identify functional groups.

1. **OH bond** in carboxylic acids = 3230-3550 cm^{-1} (wavenumber)
2. **OH bond** in alcohols = 2500-3300 cm^{-1}
3. **C=O bond** = 1680-1750 cm^{-1}
4. **C=C bond** = 1610-1680 cm^{-1}
5. **Fingerprint region.** = 400-1400 cm^{-1}

This region is too complicated to analyse, but since each molecule will give a **characteristic pattern**, it can be used to positively identify a compound by comparison with other known spectra.

A4 Mass Spectrometry (SL/HL)

From Topic 2

1. Vaporisation
2. Ionisation
3. Acceleration
4. Deflection
5. Detection

In addition to determining the **molar mass** of the substance, mass spectrometry will give some information of the structure of the molecule.

The Molecular Ion

- The ionised molecule is detected as the **molecular ion (M^+)** with the largest mass and this determines the **molar mass** of the molecule.

Fragments

- Ionisation of the molecule will often lead to the molecular ion **splitting** into **fragments**. These fragments give clues its structure.

E.g. A difference in mass between 2 fragments of ……

15 suggests the loss of a –**CH_3** group.

17/18 the loss of a –**OH/H** group.

29 the loss of **CH_3CH_2** or –**CH=O**

31 the loss of –**OCH_3**

45 the loss of –**COOH**

A5 ^{1}H NMR Spectroscopy (Low resolution) (SL/HL)

- This gives information about the **Hydrogen atoms** in the molecule.
- The nuclei of hydrogen atoms can **spin in opposite directions**. When a **strong magnetic field** is applied they may **swap the direction in which they are spinning.**
- This causes them to **absorb a small amount of energy** in the radio region of the spectrum.
- Different groups of hydrogen atoms absorb slightly different amounts of energy **depending on the chemical environment** in which they are, causing them to appear at **different positions** on the spectrum.

Some of the most common positions are:

H atoms		Chemical shift
$-CH_3$	=	0.9
$-CH_2-$	=	1.3
-CH-	=	2.0
$CH_3-C=O$	=	2.1
-OH	=	4.5
C_6H_6	=	7.3
HC=O	=	9.7
HO-C=O	=	11.7

- Generally, the more electronegative the chemical environment, the greater the chemical shift.

- The **number of hydrogen atoms** can be determined by the **area** under each peak on the spectrum.

- This is useful information as it shows how many hydrogen atoms are experiencing the same chemical environment.

Uses of NMR Spectroscopy in Body Scanners

- NMR has some very important medical applications. One reason is that the low energy radio waves used are harmless and have no known side effects.

- MRI (magnetic resonance imaging) is one application that can monitor and evaluate various medical conditions.

- It involves the whole body of the patient being placed inside the magnet of a large NMR machine.

- The protons (H's) in water, lipids, carbohydrates etc in the body give different signals that allow an accurate 3D image of the body to be obtained.

A9 NMR Spectroscopy (High Resolution) (HL ONLY)

Tetramethylsilane (TMS)

- This is used as a reference sample for the following reasons.
- It is non toxic and unreactive.
- It produces a very clear single peak since all 12 H's are equivalent.
- It is very unpolar and so occurs upfield, well away from any other possible peaks.
- It has a very low bp and so can therefore be easily removed from the sample.

Splitting Patterns

- The absorption peaks given in ^{1}H spectra are influenced by adjacent hydrogens.
- These can be analysed when using high resolution NMR to show a peak **splitting patterns**.
- Singlet: If there are no adjacent H's.
- Doublet: If there is one H atom on an adjacent carbon.
- Triplet: If there are two H atoms on adjacent carbons.
- Quartet: If there are 3 H's on adjacent H's.
- This is called spin-spin coupling. Exact details of how these patterns arise is not required.

A6 Atomic Absorption Spectroscopy (AA) (SL/HL)

Uses of AA Spectroscopy

- AA measures the amount of energy that is absorbed by electrons as they are promoted from lower to higher energy levels.

- It is the reverse of emission spectra that measure the energy released when electrons drop down into lower energy levels and give rise to characteristic colours of flames in the visible region (potassium = lilac)

- A light source of a particular frequency/wavelength is selected to complement the colour of the sample. Using the amount of energy absorbed, the **concentration** of the sample can be accurately determined.

- It can therefore be used to determine the concentration of **metal ions** in samples such as water, blood, food, soils etc.

Principles of AA Spectroscopy

- AA machines work on the same double beam principle outlines for IR spectra.

Draw a simplified labelled diagram:

- The sample is turned into a fine mist and then burnt in a fuel/air mixture. This happens in the atomizer.

- A monochromatic light source is then passed through the resulting flame. The light source needs to contain the metal under investigation so that the correct frequency of light will be used.

- The amount of light absorbed by the atoms in the sample is detected and converted into an electrical signal.

- By changing the light source, the concentration of different metals in the same sample can be determined.

Finding Concentrations

- The amount of light absorbed by a sample (Absorbance) is directly proportional to the concentration of metal ions in the sample.

- This is called the Beer Lambert Law.

$$A = \epsilon C l$$

A = Absorbance ε = molar absorbtivity coefficient (constant)

C = concentration l = path length of sample cell

$$A = \varepsilon l c$$

$$1.92 = 19400 \times 1 \times C$$

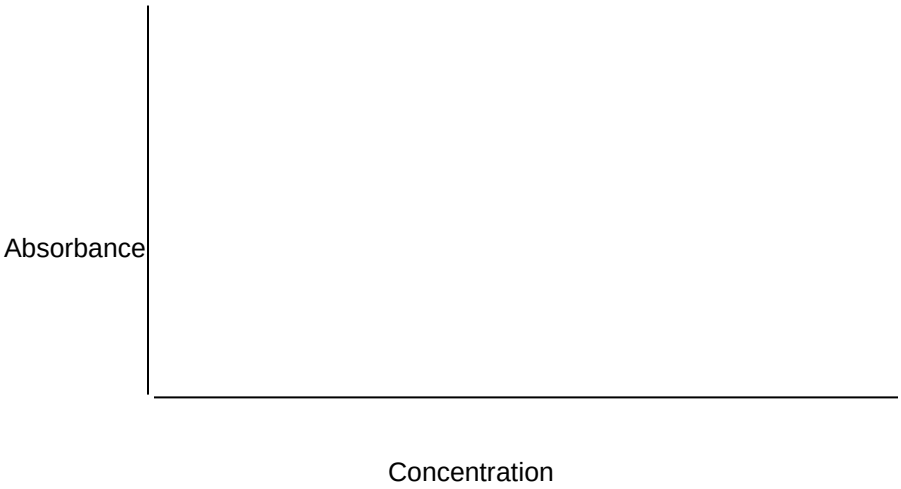
$$C = \frac{1.92}{19400}$$

$$= 9.90 \times 10^{-5} \text{ mol dm}^{-3}$$

E.g. A metal solution in a cell of length 1 cm. The absorbance of the solution at a particular wavelength is 1.92. The molar absorptivity is 19400 for that wavelength (from a data book)

Calibration Curves

- Using this relationship, if a calibration curve is determined for a particular metal using various known concentrations, the concentration of an unknown solution of that metal can be easily determined.



Note: The calibration curve and Beer Lambert Law becomes less linear at higher concentrations of solution.

A7 Chromatography

Uses of Chromatography

- Chromatography can be used to separate mixtures containing very small amounts of substances.
- It can be used to identify how pure a substance is.
- By comparisons to known samples it can be used to identify components and also determine the concentration/amount present.

Principles of Chromatography

- All types of chromatography involve separation involving two phases. The **stationary phase** stays fixed. The **mobile phase** moves.
- Separation occurs due to the difference in tendency to absorb onto the stationary phase compared to its solubility in the mobile phase.
- **Adsorption** involves a **solid stationary phase** and a **liquid mobile phase**. The distance a solute moves depends on the relationship between how quickly it absorbs onto the solid phase compared to its solubility in the liquid phase.
- The faster it absorbs, the less distance it moves.
- **Partition** involves a **liquid stationary phase** and a **liquid/gas mobile phase.** If the mobile phase is a liquid, the distance moved by the solute depends upon its difference in solubility in the two phases. If the mobile phase is a gas it depends on the volatility of the solute.
- The more soluble/volatile, the greater distance moved.

Different Types of Chromatography

a) Paper Chromatography.

- Paper consists mainly of cellulose that consists of a large number of OH groups.
- Water can H-bond to these polar groups in the paper so that 'dry' paper still consists of about 10% water.
- It is this water that is 'trapped' in the paper that acts as the **stationary phase**.
- The **mobile phase** is a solvent (eluent). E.g. water itself, ethanol etc.
- The mixture is spotted on the paper about 1cm from the base. This is marked with a pencil line.
- The paper is placed in a small volume of water below the pencil line.
- A lid is put on the container to saturate the atmosphere.
- The solvent rises up the paper and the various components separate between the two phases according to their relative solubility.
- The final distance that the solvent rises is also measured (solvent front).
- After drying, if required the components can be stained by a dye (developed) to make them visible, and then the distance moved can be measured.
- This is used to calculate the **retention factor (R_f)** and these can be compared to known values to deduce the identity of the various components.

$$\text{Retention factor } (R_f) = \frac{\text{Distance moved by solute (cm)}}{\text{Distance moved by solvent (cm)}}$$

b) Column Chromatography (LC)

- This is used to separate components in a mixture rather than identify them.
- This consists of a long column packed with a solid stationary phase (E.g. silica gel)
- The column is saturated with solvent.
- The mixture is poured in the top and separates the various components according to their solubility in the solvent.
- If necessary, another solvent can be then introduced to dissolve and separate other components that are still held in the column.

c) Thin Layer Chromatography (TLC)

- This works by the same principle as paper chromatography, except instead of the paper, a thin layer of solid (silica) is used.
- In the same way, water acts as the stationary phase and the mobile phase is another solvent.
- TLC allows the component to be scraped off at the end and re-dissolved. This method is used for some pregnancy sets.

d) Gas-Liquid Chromatography (GLC) HL ONLY

- This technique is used to analyse a mixture of **volatile liquids**.
- The liquids need to be stable at temperatures close to the boiling point.
- The stationary phase consists of a liquid suspended on a solid in a long thin tube.
- The mobile phase is an inert gas such as helium or nitrogen.
- The sample is injected and then vaporised by heat.
- The various components in the vaporized mixture are then carried through the column by the inert gas.
- Depending on the solubility in the stationary solvent, the components have different retention times and therefore reach the detector at different times.
- This method also allows the measurement of the relative concentrations using the area under the peaks. This allows for use in detecting the alcohol level in blood during drink driving tests.

e) High Performance Liquid Chromatography (HPLC) HL ONLY

- This method works in a very similar way to GLC. Instead of allowing gravity to move the components through the column, they are forced through much faster under **pressure**.
- This means that the column used doesn't have to be as long as the process is very efficient.
- As well as separation, HPLC can also be used for identification of the components present.
- HPLC is used for **non volatile substances**, and also for **volatile substances that tend to decompose near to their boiling points**. It can also be used to separate and identify **optically active compounds** if the column is prepared using another optically active stationery phase.
- Other uses include pollutants, food, alcoholic drinks, insecticides/herbicides, biochemical research and pharmaceuticals.

A8 Visible and Ultraviolet Spectroscopy (HL ONLY)

Transition Metal Complex Colours

- Transition metals have incomplete d shells. This is the main reason why they form coloured compounds. What colour are Cu^{+}, Sc^{3+} and Zn^{2+}?

- The different colours observed by various transition metal compounds depends on 4 factors.

    1. The type of transition metal.

       What are the electron configurations of Mn^{2+} and Fe^{3+}? What are the colours?

    2. The oxidation state of the transition metal.

       What is the electron configuration of Fe^{2+}? How does the colour compare to Fe^{3+}?

    3. The type of ligand.

       What colours is $[Cu(H_2O)_6]^{2+}$ compared to $[Cu(NH_3)_4]^{2+}$ compared to $[Cu(Cl)_4]^{2-}$?

       What colour is $[Co(H_2O)_6]^{2+}$ compared to $[Co(NH_3)_6]^{2+}$?

    4. The shape of the complex.

       What shape is $[Fe(H_2O)_6]^{2+}$? What shape are $[Cu(Cl)_4]^{2-}$ and $[Ag(NH_3)_2]^{+}$?

Splitting of d Orbitals in Transition Metal Complexes

- There are 5 d orbitals of equal energy but different shapes, aligned along different axis. Sketch and label below.
- During complex formation, the non-bonding electrons on the ligand are donated into empty d-orbitals.
- In an octahedral complex, the 6 ligands approach the metal ion along the x, y and z axis.
- Which 2 of the d orbitals are arranged on these axix?
- The extra repulsion between the non bonding electrons in the ligands and these electron orbitals causes two of the d orbitals to split to a higher energy. Draw out the d orbital split for an aqueous Fe2+
- Light can be absorbed by these complexes causing electron transition from the lower to the higher energy d orbital energies.

- Label the amount of splitting as ΔE. This amount of energy can be affected by the type of ligand, the oxidation state of the metal, the type of metal ion and the shape of the complex.
- NH_3 liagnds cause more splitting than H_2O, Cl^- cause even less.
- The colour seen is the complementary colour to the one absorbed. E.g. $[Cu(H_2O)_6]^{2+}$ absorbs red/orange light and so appears light blue. When some of the ligands are replaced by NH3 to give $[Cu(NH_3)_4(H_2O)_2]^{2+}$ the splitting increases and the complex absorbs energy in the yellow region. This causes the colour to appear violet/blue.

UV-Vis Spectroscopy in Organic Molecules

- Organic molecules containing alternate double bonds are able to absorb energy in the visible and UV range. These include long chain alkenes and arenes.
- Examples include retinal (vitamin A) chlorophyll and B carotene. Draw out the structure of one of these.

- This type of structure is said to contain **conjugation**.

- The part of the molecule where conjugation occurs is called the **chromophore**. Label the chromophore on the molecule above.
- Light energy can be absorbed causing the pi electrons to become delocalized and move to different orbitals. The amount of energy absorbed depends on the amount of conjugation in the molecule.

> More conjugation, more delocalization, the less the amount of energy required to excite the electrons. This means that absorption is more likely to occur in the visible region.

- E.g. Alkenes have only 1 double bond, no conjugation or delocalization. The energy required to excite the electrons into unfilled (molecular) orbitals is greater leading to absorption in the uv part of the spectrum. This is why alkenes appear colourless. (As do aldehydes and ketones).

- What colour is chlorophyll or B carotene? Do they absorb uv or visible light? What about their structure allows this to happen? Extension: What actual (complementary) colour must they absorb?

- Draw out the dissociation of the weak acid phenolphthalein.

- Explain why in acid it is colourless, but in alkali it becomes a colourful pink.

- One of the main ingredients in suntan lotions is 4-aminobenzoic acid. Draw the structure below.

- Explain why this molecule is able to absorb harmful high energy uv light.

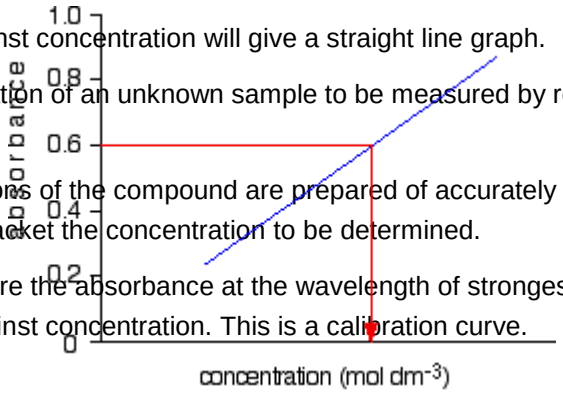
Using the Beer Lambert Law to Form Calibration Curves

- The amount of light absorbed by a sample (Absorbance) is directly proportional to the concentration of metal ions in the sample.

- This is called the Beer Lambert Law.

$$A = \epsilon C l$$

- If several samples of transition of varying concentration are prepared, the absorbance can be measured using a spectrometer/colorimeter.
- Measurements are made using (λ_{max}) by selecting the wavelength of light that is the complementary colour using an appropriate filter.
- Plotting absorbance against concentration will give a straight line graph.
- This allows the concentration of an unknown sample to be measured by recording the absorbance and comparing to the graph.
- E.g. If a number of solutions of the compound are prepared of accurately known concentration. Those concentrations should bracket the concentration to be determined.
- For each solution, measure the absorbance at the wavelength of strongest absorption (λ_{max}). Then plot a graph of absorbance against concentration. This is a calibration curve.



- According to the Beer-Lambert Law, absorbance is proportional to concentration, producing a straight line. That is true as long as the solutions are dilute, but the Law breaks down for solutions of higher concentration.
- No attempt is made to force the line back through the origin. If the Beer-Lambert Law worked perfectly, it *would* pass through the origin, but this can't be guaranteed for all concentrations.
- Measure the absorbance of the solution with the unknown concentration at the same wavelength. If, for example, it had an absorbance of 0.600, record the corresponding concentration from the graph as shown.