CH3041 Tutorial 6 Analytical B Answers

1. What property of a molecule is important for **headspace GC analysis** to be successful?

Headspace analysis is an extraction technique that relies on the volatility of the analyte. Normally applied to organic vapours above water it samples the vapour above water using a syringe through a septum which is then injected into the GC.

2. Describe how a **solid phase extraction (SPE) cartridge** works?

A solid phase extraction cartridge is essentially a very short column containing around 100 - 500 mg of the absorbent which is the stationary phase. Often the HPLC stationary phase C18-silica is used, this is a reverse phase media where C18 groups are bonded to silica spheres (around 5μm).
The cartridge must first be conditioned which involves passing MeOH (5mL) through the cartridge and then (5mL) of water through the cartridge.
The analyte of interest (an organic) in water is then passed through the cartridge and absorbs on the surface of the C18 cartridge preferentially (like dissolves like). If the material is only to be separated from water it is then simply washed with water and then eluted using MeOH. If a separation is required then gradient elution is used using MeOH/H_2O mixtures, the eluting mixtures are the mobile phase and the technique is a form of absorption chromatography.

3. Describe the difference between a **direct titration** and a **back titration** using examples.

Direct titration: the analyte of interest (unknown concentration) is found in solution in the conical flask and the reference compound (known molarity) is in the burette. The analyte reacts with the reference according to a fixed and known stoichiometry. The end point is indicated by an acid-base indicator which responds to the first drop of excess titrant past the equivalence point or a redox system is used where a colour change occurs as the titrant becomes in excess.
eg: oxalic acid (colourless) reacts with $H^+/KMnO_4$ according to the following stoichiometry:

$$5\ H_2C_2O_4 + 6H^+ + 2MnO_4^- \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

This is a good end point as the reaction is proceeding to give a colourless product and the endpoint when excess MnO_4^- becomes present will be easy to see as the excess purple MnO_4^- appears.

Back titration: the analyte of interest (unknown concentration) is found in solution in the conical flask and the reference compound (known molarity) is in the burette. The analyte is completely reacted with a known amount of a standard reagent which is added in excess. This reagent reacts with the analyte according to a known stoichiometry and with the reference compound in the burette according to a fixed and known stoichiometry. The endpoint again is indicated by a change in colour as the excess reagent is removed by the titrant. The amount of titrant is used to calculate the excess amount of the reagent present. This amount is then deducted from the initial amount of the reagent added to calculate the amount of the analyte, from the stoichiometry the amount of analyte is then determined.
eg. In the Acid Neutralisation Capacity test for acid sulphate soils an excess of acid, HCl, is added to the soil (or rock) and this reacts with all the available basic sites in the material.

$$2HCl + CaO \rightarrow CaCl_2 + H_2O$$ (here we are taking lime as a typical basic constituent)

The excess HCl is then back titrated with NaOH to determine the amount of HCl that has reacted.

$$HCl + NaOH \rightarrow NaCl + H_2O$$

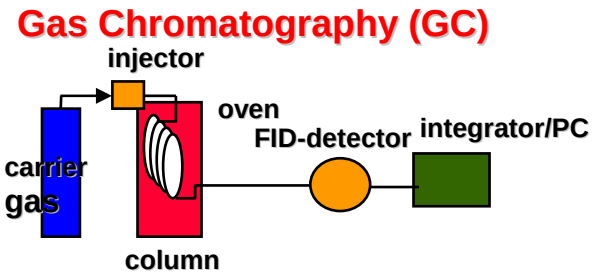
If a direct titration was used the equivalence point would not be clearly delineated. This arises as there are a variety of different basic sites in the material and it would be difficult to determine exactly where the end point is. In contrast the back titration ensures that all the basic sites have been removed by placing them in a large excess of acid, the titration then is just a normal simple 1:1 strong acid/ strong base titration.

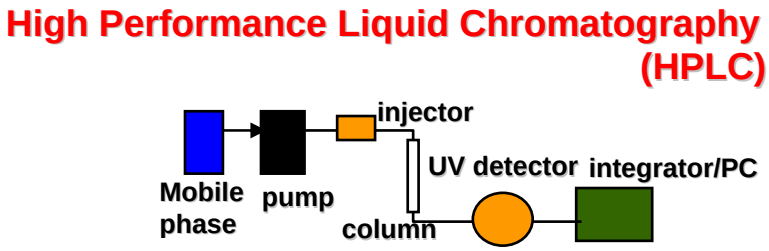
4. What is the basic physical difference between **UV-Visible spectroscopy** and **Fluorescence** spectroscopy?

UV-Visible spectroscopy is a form of absorption spectroscopy that relies on the excitation of electrons from one molecular orbital to another. The difference in energy associated with the transition is related to the wavelength of light absorbed by $E = hc/\lambda$. The wavelength range is in the UV (180-380nm) of the visible (380 - 780 nm) parts of the electromagnetic spectrum. A beam of light is shone through the sample in solution and the intensity of light transmitted is related to the absorption of the original incident beam. Used in many water analyses eg. Molybdenum blue complex formed with phosphate - colorimetry.

Fluorescence is a form emission spectroscopy where a light beam is shone on a sample and then the light emitted by the sample is measured at an angle of 90^o with respect to the incident beam. Again this is a type of electronic spectroscopy but here the incident light is used to excite the electrons to higher energy MOs from which they radiate energy according to $E = hc/\lambda$. Emissions are usually in the UV range.
Used in several gas phase analyses eg. SO_2 analysis

5. Draw schematic diagrams for **GC-FID** and **HPLC-UV/Vis** spectrometers including class of compounds each is appropriate for, details of the columns and the stationary and mobile phases which are used to enable successful separations.





The FID detector is a Flame Ionisation Detector which analyses for all organic compounds.
The HPLC uses a Ultra-Violet Detector which analyses for those organic compounds which contains a chromaphoric group.

Columns: GC 30m, Capillary open tubular 0.32mm, fused silica with Carbowax film on the surface
(N.B. this is strictly GLC). This is a form of partition chromatogrphy,
HPCL 30cm, open packed column 1mm, C18-silica 5μm is the standard reverse-phase.
This is a form of partition chromatogrphy,

Mobile phase : GC : He, the flow rate is controlled at either a constant or variable level.
HPLC : MeOH / H_2O either isocratic or gradient elution, increase the organic solvent to increase the eluent strength.