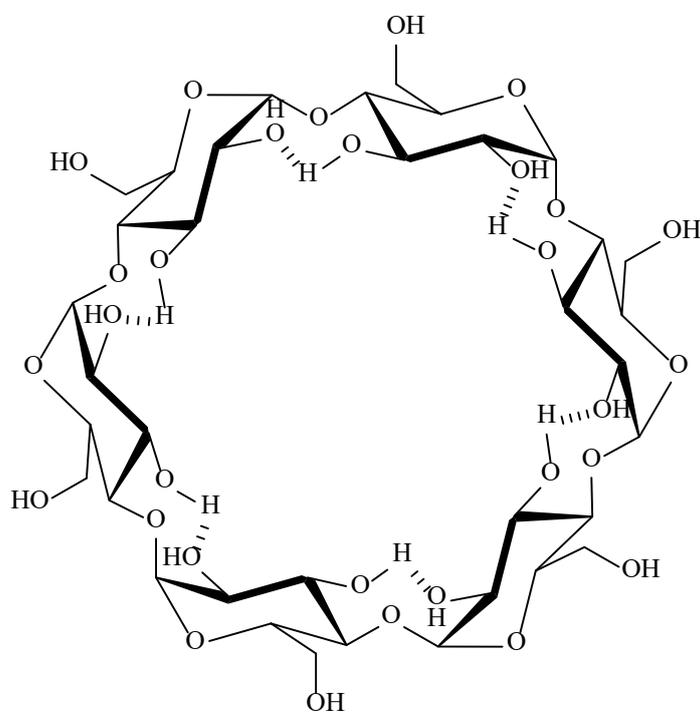


Experiment 17

Supramolecular Chemistry



The Task

The goals of this experiment are to synthesise a series of molecular framework solids and characterise their ability to selectively bind cations and to detect inclusion complex formation by an organic guest molecule.

Skills

At the end of the laboratory session you should be able to:

- use a centrifuge,
- use a UV/visible spectrophotometer,
- perform a flame test to identify a metal ion present in solution,
- carry out spot-tests and make observations,
- synthesise a molecular framework solid.

Other outcomes

You will appreciate how molecular environment influences the colour of a chemical compound.

The Assessment

You will be assessed on your correct use of the centrifuge. See Skill 11.

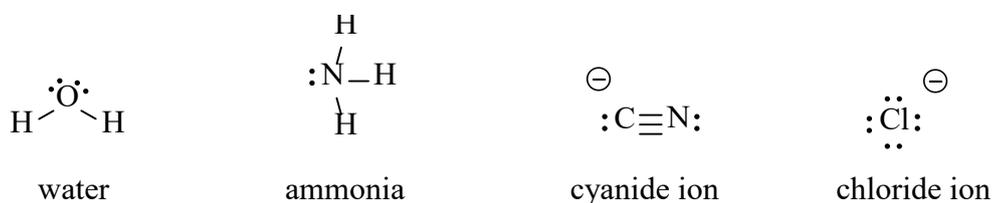


Introduction

Supramolecular chemistry is a relatively new area of chemistry. Basically, it is the chemistry of non-covalent forces, *e.g.* electrostatic interactions (such as London dispersion forces, dipole-dipole interactions, hydrogen bonds). Thus, in contrast to organic molecules which are held together by covalent bonds and inorganic solids which are held together by ionic bonds, supramolecular complexes are assemblies of smaller molecules which are stable purely on the basis of non-covalent interactions. A sophisticated example of a supramolecular assembly in Nature is a virus particle. Up to now chemists have not yet succeeded in synthesising artificial supramolecular species which are as complex as a virus, but with increasing experience more and more complex supramolecular complexes are being produced. In this experiment you will investigate examples of both an inorganic supramolecular complex (molecular frameworks) and an organic supramolecular complex (a cyclodextrin inclusion compound).

Coordination Complexes

Species that consist of a central metal ion bonded to ions or molecules are called coordination complexes. Coordination complexes are widely distributed in Nature and are found in haemoglobin (coordinating metal ion = iron), chlorophyll (metal ion = magnesium) and vitamin B12 (metal ion = cobalt). Most coordination complexes carry a net charge (either positive or negative) and they are then usually called coordination complex ions. The molecules or ions that bond to the metal in a coordination complex are known as ligands. All ligands have at least one lone pair of electrons that can bond to the metal. Typical examples are water, ammonia, cyanide ion and chloride ion.

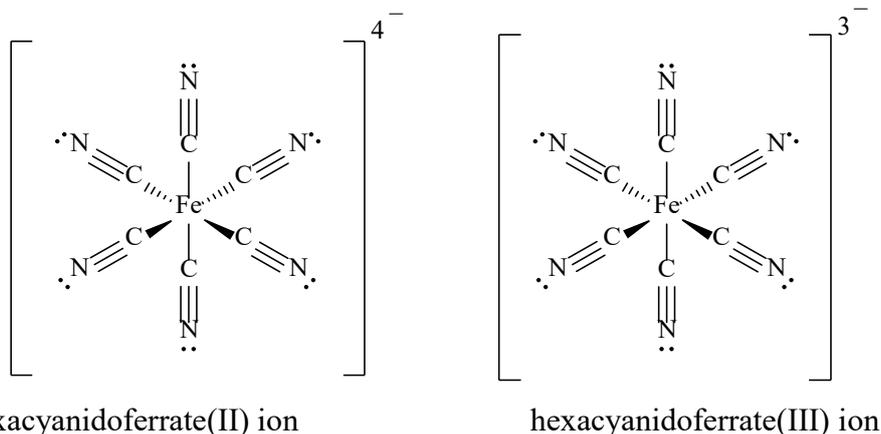


The CN^- ion forms a large number of stable complexes with transition metals (Groups 3-12 of the Periodic Table). Usually it forms just a single bond (from the carbon to the metal ion). However, it has the ability to bond through the nitrogen to a different metal at the same time. When it does this, it is acting as a *bridging* ligand.

A molecular framework solid consists of metal ions linked by organic ligands. By varying the selection of metals and the ligands that link them, it is possible to produce a wide variety of different molecular framework solids. Depending on the length of the linking ligands and the periodic arrangement of the metal ions, framework solids can exhibit a wide variety of pore sizes and properties.

Prussian Blue Analogue Molecular Frameworks

Today in the laboratory you will be making Prussian Blue and Prussian Blue analogue molecular framework solids. Prussian Blue is the pigment that gives the blue colour in blueprinting and in many paintings. It was discovered at the beginning of the 18th Century and is made from iron(II) and/or iron(III) hexacyanide complexes. The ions Fe^{2+} and Fe^{3+} are called iron(II) and iron(III), where the Roman numerals II and III are termed the *oxidation state* of the metal ion. Metallic iron, Fe, has an oxidation state of 0.



When another transition metal ion is added to the iron hexacyanide complex it can act as a ‘linker’ binding to two (or more) hexacyanide complexes and so building up an extended structure. The crystalline structure of this assembly is shown in Figure 1. The formation of crystals typically requires a very slow growth process. When a solution of the cyanide complex is mixed with a solution of the “other” metal ion, the result is an imperfect structure. These imperfect structures are interesting because, unlike crystals, they are easily made and can adopt many different physical forms. These molecular frameworks can sequester certain ions and as a result, their potential uses in environmental clean-ups and as treatments for heavy metal poisoning are active research areas.

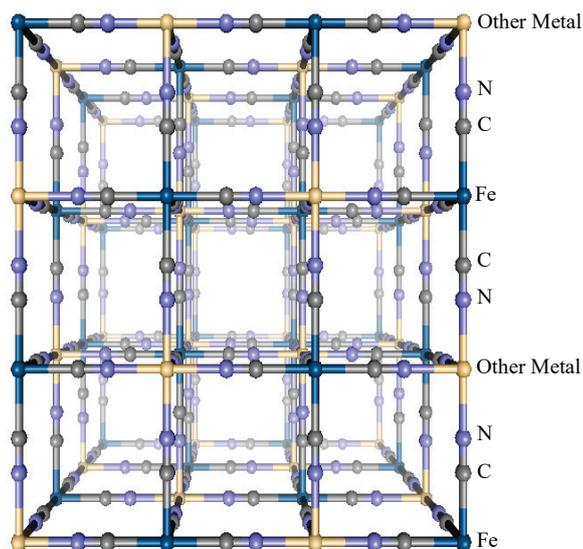


Figure 1: Nanoporous Prussian Blue analogue showing the 3-dimensional structure of the molecular framework, where the cyanide ligand forms links between the two metal ions. The metal ions on the corners and edges are connected to more cations through more cyanide links.

In simple ionic crystals, the spaces in the crystals are usually small. In contrast, the pores that are formed within a molecular framework solid are large enough to allow ions and gases to move in and out. This can confer some useful properties on the solid, some of which will be investigated today.

Cyclodextrins

Figure 2 shows the structure of glucose, the most common organic molecule in Nature. In the ubiquitous polymers starch and cellulose, the glucose monomers are joined together in 1,4 linkages. Cyclodextrins are naturally occurring cyclic oligosaccharides, consisting of glucose units connected in a ring, again using 1,4 linkages. α -Cyclodextrin contains 6 glucose units, β -cyclodextrin contains 7 and γ -cyclodextrin contains 8. All are naturally occurring. Because of their cyclic structures, they can be considered as molecular scale buckets and, as for all buckets, the cavity within the cyclodextrin molecules can be filled. Any molecule which inserts itself into the cavity is termed a *guest* molecule, and the cyclodextrin itself is called the *host*. A cyclodextrin molecule containing a guest molecule is termed an *inclusion complex*. As in the case of the inclusion of gases and ions by molecular frameworks, the inclusion of organic molecules by cyclodextrins can have numerous practical advantages, *e.g.* changes in the solubility, colour, or volatility of the guests. Some medicinal drugs, for example, are administered as cyclodextrin inclusion complexes, because in uncomplexed form their solubility would be too low to be absorbed into the body. In this experiment you will investigate the effect of cyclodextrin inclusion complex formation on the colour of an indicator.

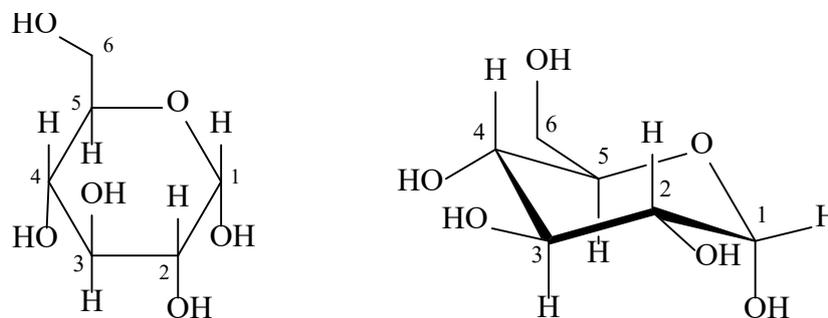


Figure 2. The glucose monomer unit. The structure on the left is greatly simplified. The representation on the right is better at showing the buckled nature of the 6-membered ring and the orientation of the H and OH groups attached to the ring. The carbon atoms are numbered according to a standard convention.

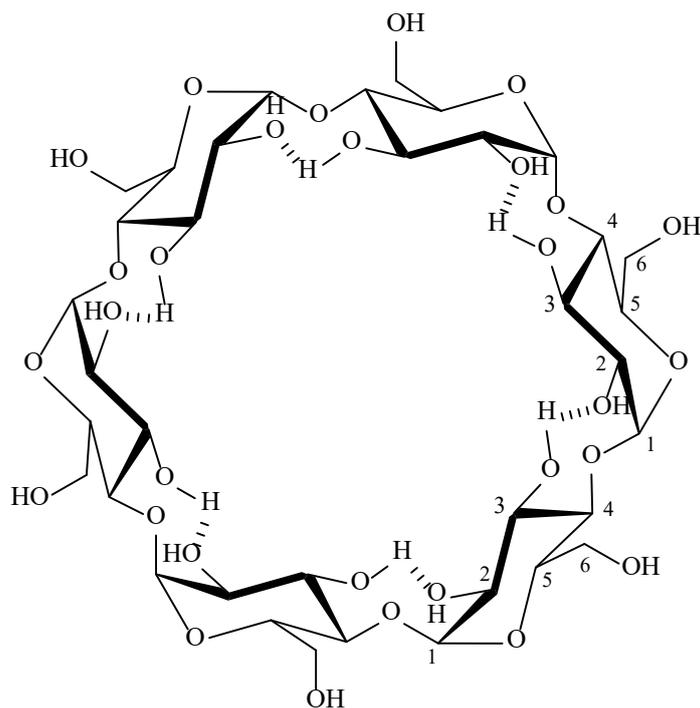


Figure 3: α -Cyclodextrin contains 6 glucose units

As shown in Figure 3, the glucose units in the cyclodextrins are all essentially parallel to each other. The OH groups attached to C6 all project downwards, away from the cavity. Similarly, the OH groups attached to C2 and C3 all project upwards, away from the cavity. They are also H-bonded to each other as shown by the dashed bonds in Figure 3. The cavity itself is hydrophobic.

Flame tests

Flame tests are explained in Skill 12. They are a very quick and simple way of determining the presence (or absence) of certain metal ions.

Centrifugation

In this experiment you will use the technique of centrifugation (Skill 11) to separate substances suspended in a liquid.

UV/Visible Spectrophotometry

In this experiment you will use the technique of UV/visible spectrophotometry to determine whether or not a guest molecule has been included by a cyclodextrin. UV/visible spectrophotometry is a spectroscopic technique for determining the wavelengths of visible or UV light absorbed or transmitted by a sample.

Safety

Chemical Hazard Identification

barium nitrate - toxic; irritating to skin.

sodium sulfate - non-hazardous.

sodium chloride - non-hazardous.

copper(II) nitrate - toxic, corrosive and a severe irritant to the eyes.

zinc chloride - highly corrosive and a severe irritant to the eyes and skin. Toxic if ingested.

iron(III) nitrate - irritant to the eyes, skin and mucous membranes. Moderately toxic by ingestion.

iron(II) sulfate - moderate toxicity, irritant to the eyes and skin.

potassium hexacyanidoferrate(II) - low to moderate toxicity and irritant.

potassium hexacyanidoferrate(III) - low to moderate toxicity and irritant.

strontium chloride - irritant to the eyes and mucous membranes.

hydrochloric acid - hazardous and corrosive. Avoid contact with skin or eyes.

methyl orange - hazardous. Irritant, toxic if swallowed.

ethanol - hazardous. Highly flammable, irritant.

α -cyclodextrin - non-hazardous

β -cyclodextrin - non-hazardous

γ -cyclodextrin - non-hazardous

Risk Assessment and Control

Low risk.

Centrifuges must be balanced. They must never be left unattended when operating as they have a tendency to walk off the edge of benches. Never attempt to stop a centrifuge with your hands - to avoid injury they must be allowed to stop naturally.

Waste Disposal

All compounds used in Parts A and B should be disposed of in the marked Heavy Metal Disposal containers located in a fume hood.

Experimental

This experiment is to be carried out pairs

Part A Precipitate or membrane? The physical character of the framework solids.

In this part of the experiment you will observe and describe the products of a variety of combinations of hexacyanide complexes and metal ions.

You will need a clean spot-test tray and a magnifying glass.

Table 1: Table of metal salts and iron hexacyanide complexes provided.

	$\text{Cu}(\text{NO}_3)_2$	ZnCl_2	$\text{Fe}(\text{NO}_3)_3$	FeSO_4
$\text{K}_4[\text{Fe}(\text{CN})_6]$				
$\text{K}_3[\text{Fe}(\text{CN})_6]$				

(A1) **Copy Table 1 into your logbook** and write down the oxidation state of the transition metal ion immediately below each of the 6 formulae provided. The formulae of all common anions and cations found in this laboratory course can be found on the last page of the Skills section of this manual.

(A2) In a clean spot-test tray make up the 8 combinations of hexacyanide/metal ion indicated by the grid in Table 1. Use two drops of each 0.25 M solution and add them gently so that the two solutions **do not mix** - you are interested in any reaction that happens at the interface of the 2 solutions. Make sure you clearly label the contents of each well. You may want to draw a larger version of Table 1 to place under the spot-test tray. Wait 3 minutes for any reaction to be completed.

(A3) In an empty well add two drops each of the 0.1 M $\text{Ba}(\text{NO}_3)_2$ solution and the 0.5 M Na_2SO_4 solution. This should cause the precipitation of insoluble BaSO_4 .

(A4) Use the magnifying glass to examine any solid material formed in (A2) and (A3).

For your logbook:

For each of the 9 wells, record the appearance and colour of the solid formed using one of the following four descriptors: a) no solid was formed, b) a finely dispersed powder, c) a coarse dispersion of aggregates, or d) a complete membrane (i.e. resembling a creased tissue). Include in your logbook how the framework solids differed in appearance from the crystalline precipitate of BaSO_4 .

Part B Selective ion binding by inorganic membranes

In this section of the experiment you will investigate whether an inorganic membrane formed from $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $\text{Cu}(\text{NO}_3)_2$ can **selectively** absorb cations, *i.e.* preferentially bind one cation more strongly than another. You will use a flame test on the solution as a qualitative test of whether or not an ion has been removed from solution.

(B1) Take three clean micro test-tubes. Add 0.25 M $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution to each to a height of ~ 1 cm. Next, to each test-tube, add 0.25 M $\text{Cu}(\text{NO}_3)_2$ solution so that the volume of liquid now comes up to a height of ~ 2 cm. Mix thoroughly with a glass rod and allow to stand for 5 minutes.

(B2) To one of the test-tubes add 0.1 M NaCl so that the total height of the solution is ~ 3 cm and mix thoroughly. (Use a stirring rod or flick the bottom of the test-tube whilst loosely holding the top. *Do not* shake with your thumb or finger over the top of the test-tube.)

(B3) To the second test-tube add 0.1 M SrCl_2 so that the total height of the liquid is the same as in (B2). Mix thoroughly.

(B4) To the third test-tube add 0.1 M BaCl_2 so that the total height of the liquid is the same as in (B2). Mix thoroughly.

(B5) Allow the test-tubes to stand for a minute, label them and place into **alternate** arms of a centrifuge, so that the rotor is balanced. Read Skill 11 on centrifugation, especially the safety aspects. Spin the tubes at half-maximum speed for 5 minutes. After spinning, any solids should be on the bottom of the test-tube as a *pellet* and the liquid above (the *supernatant*) should be clear.

(B6) Take three more clean micro test-tubes and put ~ 1 cm of 0.1 M NaCl in one, ~ 1 cm of 0.1 M SrCl_2 in another and ~ 1 cm of 0.1 M BaCl_2 in the third.

(B7) **Taking care not to disturb the solids**, carry out flame tests (Skill 12) on the solution in each of the 6 test-tubes as described in (B8) below. You need to compare the intensities of the flame emissions due to Na^+ , Sr^{2+} and Ba^{2+} from (B5) with those from the solutions in (B6), so perform the tests in a sensible order.

(B8) Take a platinum wire and clean it by dipping in 10 M HCl and then rinsing with deionised water. Dip the wire into the solution to be tested and then place into the luminous blue part of a Bunsen burner flame. The colour of the flame produced is indicative of the metal ion present (see the table in Skill 12). *Remember to clean the wire between tests.*

For your logbook:

Record the colour of the flame and its relative intensity for each sample. You will have to estimate the relative intensities by observing and recording the shape of the flame and the length of time it persists.

Did you observe any depletion in intensity of the flame emission of the Na^+ , Sr^{2+} or Ba^{2+} ions after reacting them with metal frameworks?

Part C Solvent effects on the absorbance of light

In part D of this experiment the aim is to use UV/visible absorption spectrophotometry to determine whether or not methyl orange, a pH indicator, can form an inclusion complex with a cyclodextrin. The basis of this determination will be whether or not the UV/visible absorbance spectrum of the methyl orange changes on adding the cyclodextrin. By binding within the cavity of the cyclodextrin, the chemical environment of the methyl orange changes, and this can cause its spectrum to change. To understand the basis of this phenomenon, let's first investigate what effect the chemical environment has on methyl orange simply by changing the solvent.

The measurements will be made with a UV/visible spectrophotometer which is located in the Instrument Room at the back of laboratory C. Full operating instructions for these instruments can be found in the Appendix of this experiment (page E8-13). Other important considerations are:

- Handle the cuvettes by the opaque sides only – do not touch the transparent windows of the cuvettes. Finger smudges on the transparent windows could be recorded by the instrument as an absorbance.
- Make up all solutions in the main laboratory – fill and empty cuvettes before entering the instrument room. **Do not make a mess in the Instrument Room.**

(C1) Make sure the spectrophotometer is turned on. (The lab staff should have already done this.) It takes about 10 minutes to warm up.

(C2) Perform a baseline correction as follows. Insert a cuvette containing 1.5 mL of ethanol into the cuvette holder of the instrument. Set the wavelength range to 600 to 300 nm. Push F1. It takes several minutes for the instrument to perform a baseline correction. Don't stop it before it's finished.

(C3) Add 0.03 mL (one drop) of the 2×10^{-3} M aqueous solution of methyl orange to the cuvette used in (C2) and mix the solution by inverting a couple of times, making sure you have covered the top of the cuvette with Parafilm. Record an absorbance spectrum of methyl orange in ethanol. If the absorbance overflows (is "maxed out"), no reading is possible and you need to dilute the sample and try again. **Record your observations in your logbook**, particularly the wavelength where the absorbance maximum occurs.

(C4) Repeat steps (C2) - (C3) using deionised water as the solvent instead of ethanol.

For your logbook:

Did you observe any difference in the wavelength of maximum absorbance for methyl orange in ethanol and water?

Does a decrease in polarity of the medium shift the absorbance spectrum of methyl orange to shorter or longer wavelengths? (Hint: Consider the relative polarities of water and ethanol and your answer to the previous question.)

Part D Selective molecular binding by cyclodextrins

In this part of the experiment you will determine which of α -, β - or γ -cyclodextrin is best able to complex methyl orange.

- (D1) Fill a cuvette with 1.5 mL of the 1×10^{-3} M aqueous solution of α -cyclodextrin.
- (D2) Add 0.03 mL (one drop) of the 2×10^{-3} M methyl orange solution to the cuvette and mix as instructed in step (C3).
- (D3) Record the UV-visible absorbance spectrum of the solution over the range 600 to 300 nm. **Record your observations in your logbook**, particularly the wavelength where the absorbance maximum occurs.
- (D4) Repeat steps (D1) - (D3) using the 1×10^{-3} M aqueous solution of β -cyclodextrin.
- (D5) Repeat steps (D1) - (D3) using the 1×10^{-3} M aqueous solution of γ -cyclodextrin.

For your logbook:

Which cyclodextrin gave you the biggest shift in the wavelength of maximum absorbance relative to methyl orange in water? Thus, which cyclodextrin do you think is best at complexing methyl orange? Comparing your results from parts C and D, do you think the environment of the cyclodextrin cavity is more like water or ethanol?

Group Discussion

Did you observe a selective ion absorption by the framework solid? If yes, what properties of the ions might have been responsible for their different degrees of binding?

What were some of the physical differences you observed between the framework solids and an ionic solid like BaSO_4 ?

The absorbance of light by any molecule causes it to undergo a transition from a ground state to an excited state (with a different distribution of its electrons). Water, H_2O , is a polar molecule which can interact with methyl orange in both the ground state and excited electronic states, causing a stabilisation (*i.e.* lowering of energy). Comparing your wavelengths of maximum absorbance for methyl orange in ethanol and water, do you think that water has a stronger interaction with methyl orange when it's in an excited state or a ground state? Hint: Remember that energy is inversely proportional to wavelength?

Did you observe selective binding of methyl orange by the cyclodextrins? If yes, what property of the cyclodextrin might have been responsible for the different degrees of binding?

References

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Appendix 17.1

Operating Instructions for the SHIMADZU UVmini-1240 (Room 218)

THE CUVETTES

1. Two special cuvettes will be issued to you by your demonstrator.
2. They are made of silica and are transparent to UV radiation. They are fragile and expensive so handle them with care. Handle them by the opaque sides only - do not touch the transparent windows of the cuvettes.

START UP

1. Switch on via the power switch located on the back of the instrument.
2. Allow the spectrophotometer to warm up (up to 10 minutes).
3. When the instrument is ready, a list of the instrument's functions, titled "Mode Menu" is displayed on the screen.
4. Press **2** on the keypad to select spectrum measurement mode. The following reminder appears:
Caution!
Please correct baseline data before measurement.
5. Press **Enter** to proceed.

CHANGING PARAMETERS

1. To change between absorbance (ABS), % transmittance (T%) or energy (E) measurement modes, press **1** to display the menu containing the options: ABS, T% and E. Use the \uparrow and \downarrow arrow keys to select the absorbance mode, then press **Enter**.
2. To select the wavelength range of 600 nm - 300 nm, press **2** and then key in **6** **0** **0** **enter** followed by **3** **0** **0** **enter**.

BASELINE CORRECTION

1. For baseline correction, place the blank sample (*i.e.* the cuvette filled with solvent only) into the instrument and press **F1** to measure the baseline.

SAMPLE MEASUREMENT

1. After the instrument indicates that baseline measurement is complete, replace the blank with the sample to be measured and press **Start/Stop** once.
2. The printer automatically prints the spectrum after each measurement.
3. To re-print the spectrum, press **Print** while the spectrum is still displayed on the screen.

INSTRUMENT SHUTDOWN

1. If you are the last person to use the instrument for the session, make sure it is switched off, firstly at the back and then at the mains.

Make sure both cuvettes have been rinsed clean and returned to your demonstrator.