

## Developing practical chemistry skills by means of student-driven problem based learning projects

### Supplementary Material

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### **Example project 1: “Who killed Mrs Bernhard Schneider?”**

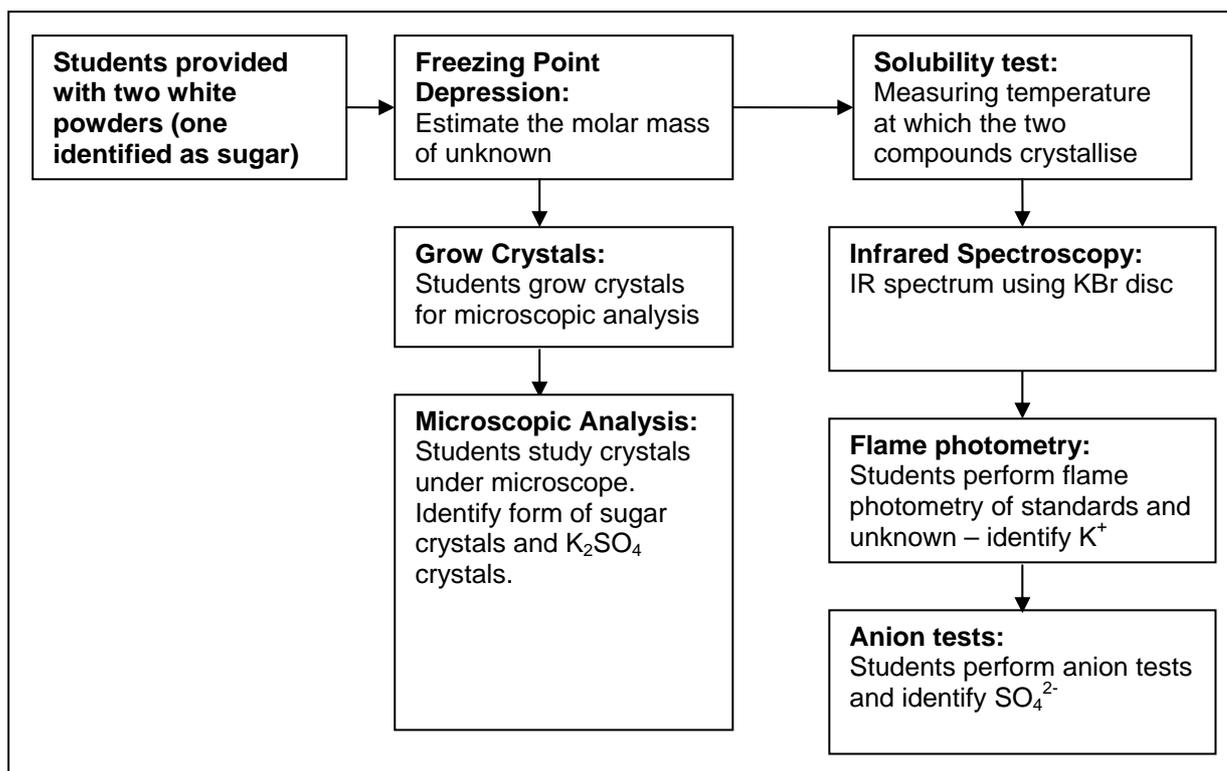
#### **Background**

This project is based on the Sherlock Holmes series published in *J. Chem. Ed.*, 2005, **82**, 1532–1533, although our results here expanded on that paper's already excellent suggestions. Interested readers are referred there for full details of the contextualised story. The authors of that paper recommend that students carry out a flame test, adding calcium chloride to the unknown, examining the crystal structure under a magnifying glass and determining the molar mass by freezing point depression.

Students are given a scenario whereby they have to identify an unknown white powder. They are first required to verify that it is not sugar, and then are required to determine what the powder is. Students are provided with a vial of sugar and a vial of the unknown (potassium sulfate).

#### **Experimental**

The following flow chart indicates the work completed by the group who undertook this project at Dublin Institute of Technology and the order in which they completed it. Students identified freezing point depression, solubility and anion tests as useful experimental methods themselves, and on prompting, identified microscopic analysis and infrared spectroscopy as additional methods. The students wished to carry out flame tests (as they had done this experiment in the first year of their course), and were informed at that stage that flame photometry apparatus was available.



### Sample Results and Findings

#### *Freezing Point Depression*

The group completed a freezing point depression experiment by measuring the freezing point of water on dissolution of the unknown salt. Although they carried out the experiment correctly, they decided to use a thermometer with 1°C graduations, which was not precise enough for this experiment. This in itself was a useful lesson, however, and the calculated molar mass for the unknown was found to be 309 g mol<sup>-1</sup>. ( $M(\text{K}_2\text{SO}_4) = 174 \text{ g mol}^{-1}$ )

Although the experiment was not a success in terms of finding out the molar mass of the compound, the group did learn some valuable lessons about choosing the correct apparatus for the experiment and the determination of experimental error.

#### *Solubility Tests*

The background story mentions that crystals were found in the bottom of a teacup. All members of the group tested this with sugar at home, i.e. made tea, put in sugar and examined it several hours later. They reported that the sugar did not fall out of solution, whereas the unknown did. In the lab, they conducted a solubility test by adding an amount of sample in increasing amounts of water, heating it to dissolve, and cooling to observe the crystallisation temperature. From these tests, they qualitatively determined that the two samples were different, based on their different solubilities.

#### *Infrared Spectroscopy*

The group was encouraged to think about the nature of the compound – whether it was inorganic or organic. They proposed that it was an ionic, inorganic compound. When pushed as to how they could verify that (by arguing that sugar dissolves in water and it is an organic compound), they decided that infrared spectroscopy would tell them more about the compound. They obtained a spectrum of both samples, and concluded that the unknown was an inorganic compound on the basis that there were no 'organic' stretches in the spectrum (e.g. C-H).

### *Flame Tests*

Once they had decided that the unknown was an ionic salt, the group decided to use flame tests to identify the cation. The flame photometer was demonstrated to them. They made up solutions of LiCl, KCl and NaCl (the three filters on the flame photometer) and observed how the apparatus worked by switching between filters. They then ran a sample of their unknown, and identified it as  $K^+$ . The flame photometer gives a concentration response. The group were encouraged to think about whether they could use the value they obtained in any way. They deduced (after much prompting!) that they could use it to work out the molar mass of the compound, knowing the mass they weighed out and the concentration reading they obtained, although they did not present these calculations in their final report.

### *Anion Tests*

The group did the various tests for anions (silver nitrate for halides; HCl and phenolphthalein for hydrogen carbonates; iron (II) sulfate for nitrates; and barium chloride for sulfates and sulfites – distinguished by adding HCl, where for sulfates, the white precipitate does not dissolve in the acid.) From these tests, they concluded that the anion was sulfate, and the salt was  $K_2SO_4$ .

### *Crystal Analysis*

The group was encouraged to think about the shape of their crystals. In our laboratories, we have a polarising light microscope. On examining the crystals, they found that the sugar crystals were cubic (“big square clear crystals”), which did not change colour on changing the polarisation of the light (i.e. are isotropic), whereas the  $K_2SO_4$  were rectangular (“longer shape, thinner crystals”), which changed colour on changing the polarisation of the light – indicating more than one refractive index.

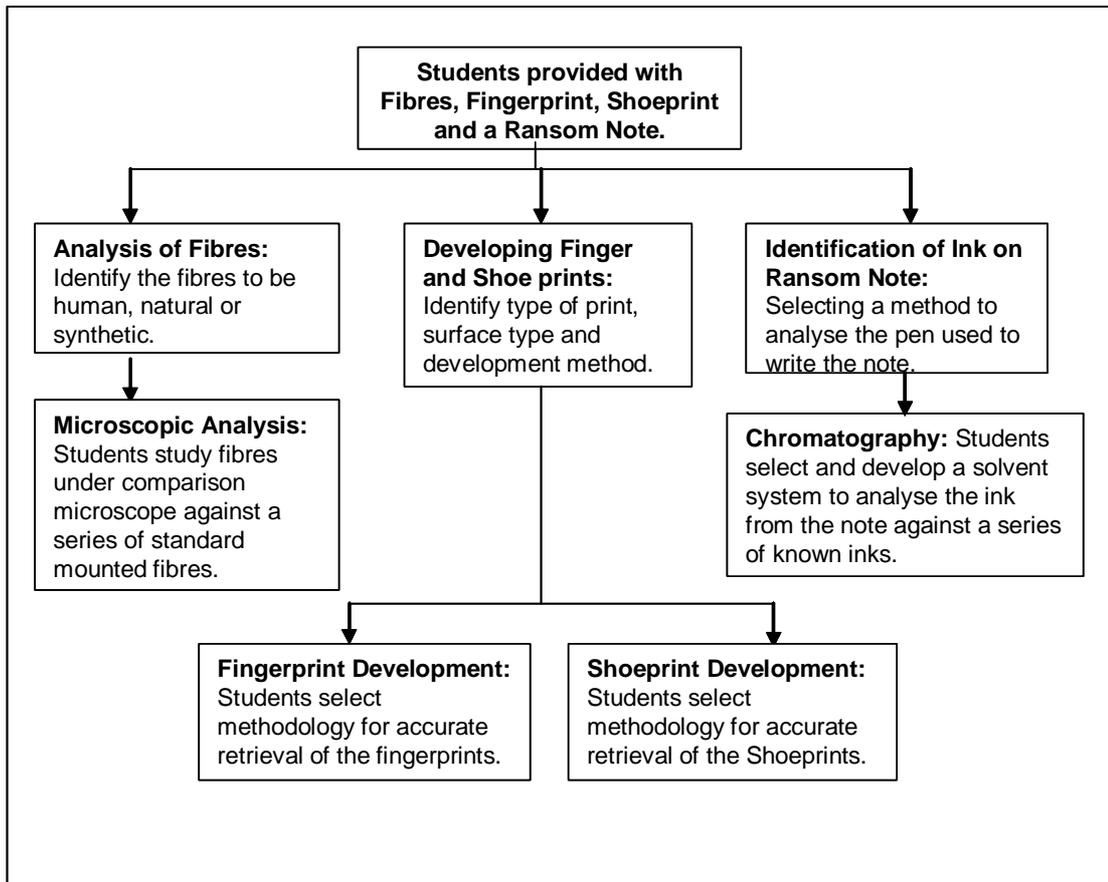
## Example project 2: “Do the forensic tools on CSI really exist?”

### Background

The group were posed the question “Do the Forensic Tools on CSI really exist?”. CSI (Crime Scene Investigation) is a popular American television show and the students were asked to compile the types of investigation carried out during the television show and recreate that environment within the college laboratory. The students received several items of evidence such as fibres, fingerprints on various surfaces, shoeprints and a ransom note.

### Experimental

The work carried out by the group is highlighted in the chart below. The experiment was designed by the students and none of the methods of analysis had been carried out as part of their curriculum prior to this project. The students identified the techniques required for analysis and devised a plan of action in order to investigate the evidence. The students incorporated the use of the comparison microscope and compared their fibres against a databank of standard fibre slides. They also designed a TLC system for the identification of inks and selected a series of forensic methodologies for the retrieval of finger prints and shoeprints.



### Sample results and findings

#### *Comparison Microscope*

The group compared their fibres with a series of standard fibres and experienced the process of fibre identification by visual comparison of the thickness, coarseness and colour of the fibre. The fibres identified were human hair, dog hair and wool.

### *Chromatography*

The students had to decide how they would compare the ink on the ransom note with a series of inks from various pens found at the scene. The unknown ink was extracted from the ransom note. The method selected was TLC (Thin Layer Chromatography) and a solvent system was developed for the identification of the ink against the pens found at the scene. The time required to develop the solvent system and choice of solvent for this analysis helped students to realise the work required in developing suitable solvent systems for chromatography.

### *Fingerprint Development*

The students had to devise a method to retrieve fingerprints from a variety of surfaces. They first had to decide whether the surface was porous or non-porous and then chose suitable development techniques. The methodologies selected were superglue fuming, iodine fuming, magnetic powder dusting and fluorescent powder dusting. The fingerprints were analysed and compared under the microscope. Fluorescent fingerprints were analysed under the UV lamp.

### *Shoeprint Development*

A method to retrieve shoeprints from a variety of surfaces had to be devised. The group first had to identify the surface and then choose a suitable development technique. The methodology selected for the shoeprints was magnetic powder dusting and adhesive lifts. The shoeprints were analysed visually for tread and wear marks. By photocopying the developed adhesive lift of the print onto an acetate sheet and overlaying that onto the suspects' shoeprint a direct comparison could be made.

### **Example Project 3: “Can the active pharmaceutical ingredients in a range of analgesic products be extracted, separated and characterised?”**

#### **Background**

Students were supplied with packets of four different over-the-counter analgesic products ( In this case, Anadin™, Nurofen Plus™, Solpadeine™, and Codis™). They were told that the active ingredients to be extracted, separated and characterised are aspirin, caffeine, codeine, ibuprofen and paracetamol. They were directed to meet with the project supervisors for some guidance before beginning to prepare their project plan.

#### **Experimental**

As a guide, the students were supplied with a list of objectives that the problem had been broken down into as follows;

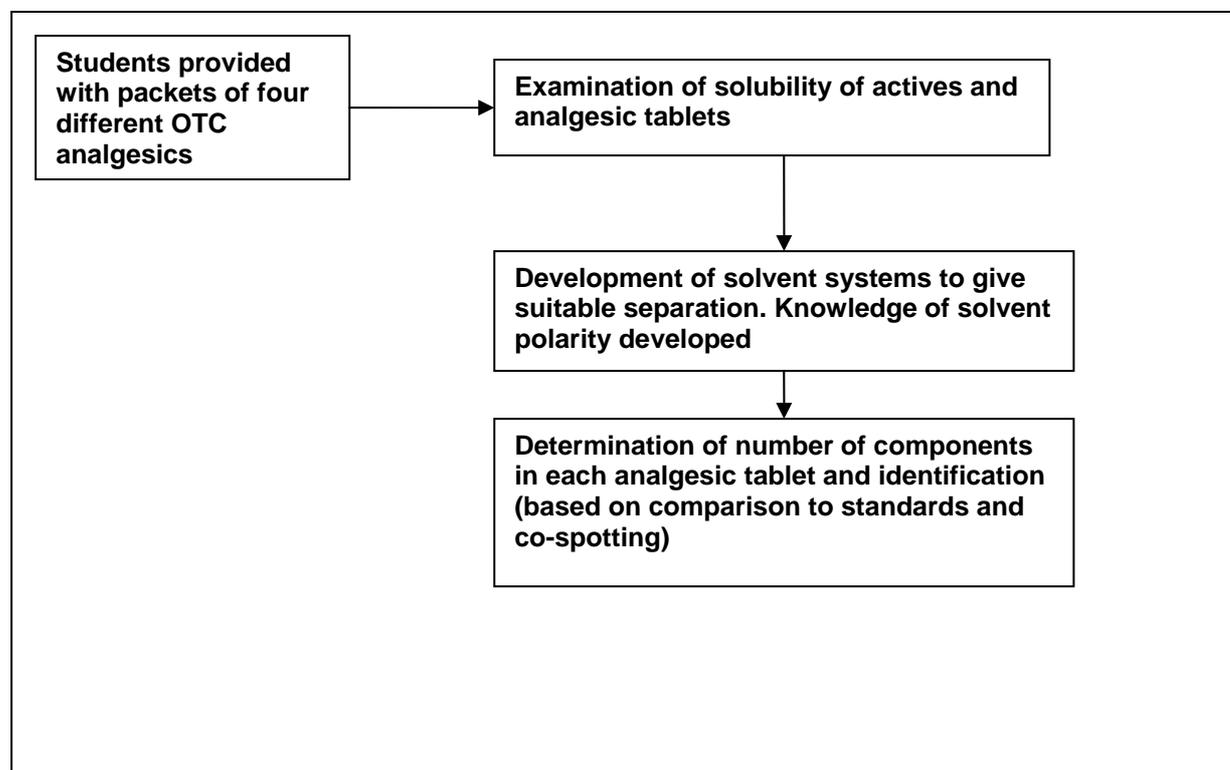
- Study the information literature available with the given medications provided and determine the active ingredients and any other organic compounds used as 'fillers' (also called excipients).
- Consult the literature and determine the structures and the physical, chemical and biological properties of these 'actives' and organic compounds.
- Obtain the MSDS data on the actives and any organic compounds used as fillers.
- Familiarise yourselves with chromatographic separation techniques, by referring to books, journals, internet and video sources.
- Consult the literature and prepare draft experimental method(s) for separation of actives from other compounds in the formulations by thin layer chromatography.
- Obtain pure samples (to be used as reference materials) corresponding to the active ingredients and the organic “fillers”, (where these samples are available).
- List all equipment and chemicals which may be needed.
- Obtain MSDS data which has not already been obtained (e.g. for solvents to be used)
- Develop conditions suitable for separation of the ingredients in each given analgesic. (Type of thin layer plates, solvent systems, development methods etc.....)
- Demonstrate clearly that each active component can be separated from the drug sample supplied and can be identified.
- Obtain a 500 mg sample of the **main active** from each of the four proprietary drugs supplied by extracting it from the medicine and recrystallising it as appropriate.
- Characterise each recrystallised active by obtaining a melting point, mixed melting point and infrared spectrum.

It was pointed out to the students that they might not achieve all of the objectives listed in the time allocated and that the important thing was that they worked consistently and could show that they were following a logical path as the project progressed.

#### **Experimental**

The following flow chart indicates the work completed by the two groups who undertook this project at Dublin Institute of Technology and the order in which they completed it. Some minor differences in the approach of each group will be mentioned but, in general, both groups undertook much the same experimental work and reached the same stage.

Initially, the students reviewed the chromatographic separation techniques that could be used in their project based on their lecture notes and opted for TLC because it was simple, quick, inexpensive and didn't require specialised equipment. They were directed to look at a video on TLC analysis available in the Library at this stage (Practical chromatography for A Level : Thin layer chromatography, University of Liverpool)



## Sample Results and Findings

### *Solubility of actives and of analgesic tablets*

The group looked up the structures and physical properties of the actives and selected a suitable solvent based on the solubility data they obtained. The effect of the excipients present in each tablet on solubility also had to be considered. The extent to which compounds with similar structures and functional groups exhibited similar solubilities was pointed out at this stage.

### *Development of Suitable Solvent Systems*

The first group in 2005 worked from first principles to develop a solvent system. They began with 100% dichloromethane and added solvents that were more polar (ethanol) or less polar (cyclohexane) to the mobile phase as appropriate

The second group in 2006 opted to use a solvent system recommended for TLC analysis of analgesics in a practical chemistry textbook (50:50 propanone:dichloromethane). They investigated the effect of increasing the percentage of polar and nonpolar solvent to ensure they had the optimum separation and found that this was the case.

In each case, the students gained an understanding of the relative polarity of common organic solvents and the effect of changes to the polarity of the mobile phase on the separation achieved. The students also developed their TLC

techniques (spotting, sample and mobile phase preparation) sufficiently to be able to achieve reproducible results.

*Determination of number of components in each analgesic tablet and identification*

Once separation had been achieved, the group set about identifying each component by analysing reference standards for caffeine, aspirin and paracetamol by TLC. Standards for codeine and ibuprofen were not available and are quite expensive to purchase. This meant that the students had to work out which spot corresponded to these components by a process of elimination. In addition, it was found that codeine was present in significantly smaller quantities (10 to 20 mg) in the tablets compared to the other analgesics (usually 100 to 300 mg) and this meant that when a spot for codeine was expected it was often faint and sometimes not visible. These two factors gave the students an indication of the type of issues that arise in "real life" problem solving situations.

Some co-spotting was also performed to check whether spots with similar  $R_f$  values represented the same substance.

Neither group of students achieved the objective of isolating a pure sample of the main active from tablets by recrystallisation and then characterising it. However, the supervisors were satisfied that they made steady progress in their work and developed their lab techniques and skills considerably.

In addition to the video on TLC analysis used, other useful references for this miniproject were;

Website with interactive tutorial on TLC;

<http://www.chem.ualberta.ca/~orglabs/chrom.htm>

Textbook with guidelines for TLC;

Advanced Practical Organic Chemistry by Leonard, Lygo and Procter, Stanley Thornes Ltd., 1998