Chemistry
Starter Investigations
(Advanced Higher)

7134

Summer 2000

HIGHER STILL

Chemistry

Starter Investigations (Advanced Higher)

Support Materials

RS•C
ROYAL SOCIETY OF CHEMISTRY

CONTENTS

* Appeared in a different format in 'Starter Projects for Sixth Year Studies', AH Johnstone in association with S Akhtar, C Gray, C Pollock. Centre for Science Education, University of Glasgow and Royal Society of Chemistry, Education Division (Scotland). (1993) ISBN 0 85261 422 5.

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ACKNOWLEDGEMENT

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INTRODUCTION

In common with all Advanced Higher science subjects the National Course Specification for Advanced Higher Chemistry includes a 20-hour investigation unit. Details of unit and course assessment requirements for the Chemistry Investigation are to be found in the unit and national course specifications for Advanced Higher Chemistry published by SQA. Further advice on assessing the Chemistry Investigation is provided in the National Assessment Bank materials for the Chemistry Investigation unit and in the guidance for external assessment of the investigation, both published by SQA.

Investigative work can be highly motivating for students. They can experience ownership of their work and have the opportunity to discuss their ideas and findings with teachers/lecturers and other scientists. All of this is to be encouraged as a valuable dimension to their learning and personal development.

The Starter Investigations

The starter investigation materials are designed to assist students in the planning stage of the investigation. Students should also be referred to the candidate's guide in the National Assessment Bank material for the Chemistry Investigation, which specifies the record of the planning process that has to be kept for assessment evidence.

The starter investigations comprise a number of sections, usually an investigation brief, some starter questions, possible investigations, some sources of information and help and hints. It should be noted that some of the starter investigations do not contain all these sections.

The investigation brief contains a short discussion of some aspect of chemistry. Sometimes the investigation brief will be about a topic the student will have previously met (e.g. electroplating); sometimes the topic will be new (e.g wine analysis). This section leads naturally into some starter questions, which poses some questions, which can be asked of the investigation brief. In answering these questions, the student will gain a fuller understanding of the topic or sometimes an idea for an investigation. Possible investigations give some suggested areas for research arising from the topic under discussion. Help and hints gives outlines of the techniques the pupil could apply to the suggested possible investigations. Some sources of information contain specific references or more background.

The starter investigations offer teachers/lecturers a variety of options in supporting students to develop a plan for their investigation. One model of using the starter investigations is suggested below, the same model is also used in the Students Guide.

Students could select starter investigations of interest from the list of titles and narrow down their choice from reading the investigation briefs. Alternatively the flow chart of areas of interest from the *Guide for Students* could be used to aid selection. Teachers/lecturers will wish to ensure that they have sufficient resources for the starter investigations they present to students.

Once a starter investigation has been selected the starter investigation can be presented to the student in a number of ways, for example:

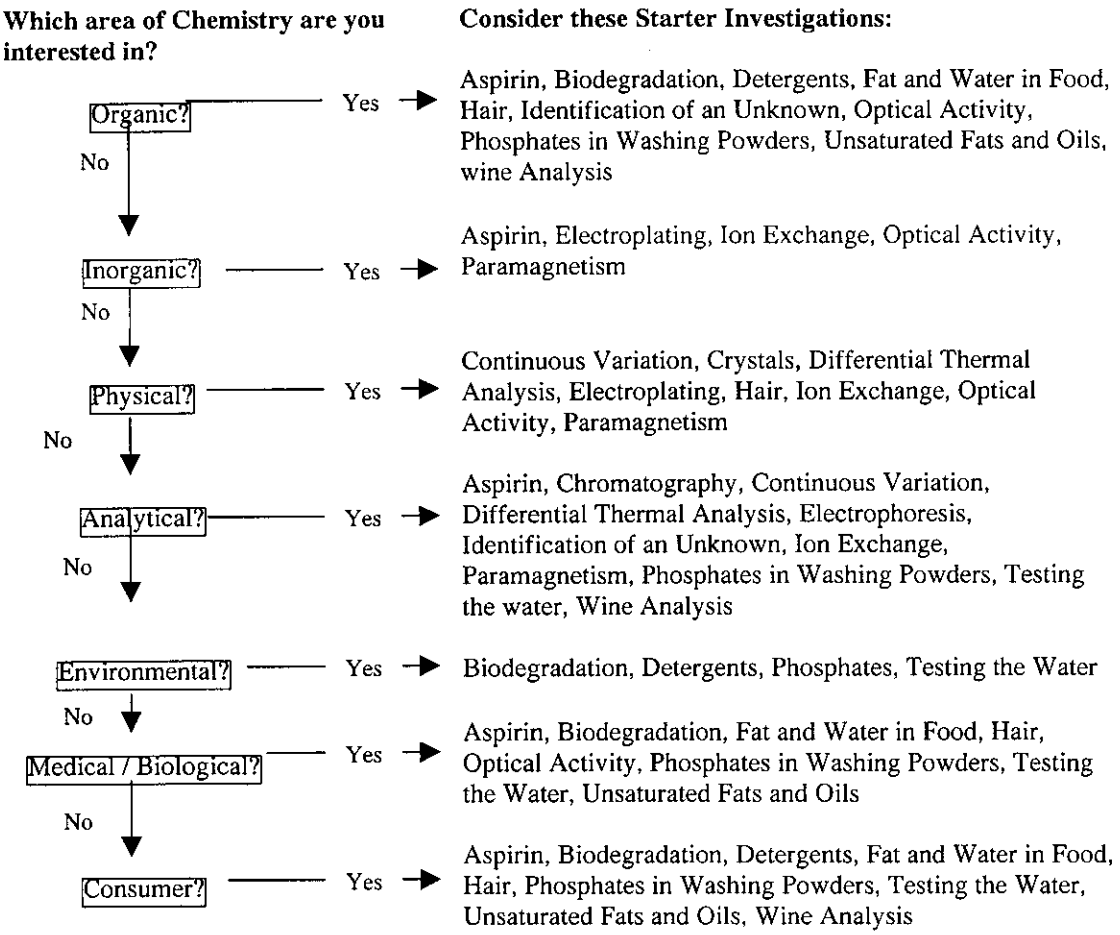
- After reading the *investigation brief*, students may be able to generate questions to investigate
- After reading the *investigation brief*, students may be able to generate questions to investigate with the assistance of the *seven step model* (appendix 1)
- After reading the *investigation brief*, students may be prompted by using *some starter questions*
- After reading the *investigation brief* and *some starter questions* students may be able to generate questions to investigate using *possible investigations*.
- The *help and hints* section may be used to assist in devising experimental procedures once questions to investigate have been developed.

It is appropriate for teachers/lecturers to support students in developing their plan using these materials. A flow chart, which can be used to support this process, is shown in appendix 2.

STARTER INVESTIGATIONS – A GUIDE FOR STUDENTS

Advice on choosing an investigation for Advanced Higher Chemistry is to be found in the National Assessment Bank materials for the AH Chemistry Investigation unit. These materials include a Guide to Candidates which you should read. The *Starter Investigations* are not a set of instructions for an investigation, rather they are a source of ideas from which you can develop your own unique investigation.

You may wish to browse through the starter investigations, alternatively you could use the flow chart below to help you select some starter investigations of interest.



Once you have selected a Starter Investigation you should discuss your ideas for an investigation with your teacher/lecturer. Your teacher/lecturer may structure this discussion with you by giving you the *Investigation Brief* and then encouraging you to think about it by posing the questions in the *Seven Step Model*. As you develop your ideas your teacher/lecturer may give you further help by giving you *Some Starter Questions*, *Some Sources of Information*, *Possible Investigations* or *Help and Hints* from the starter investigation.

As you develop your plan you must keep a record of what you are doing. At this point you should consult the advice in the Candidates' Guide from the National Assessment Bank materials on *Outcome 1: Planning your investigation*.

SAFETY ADVICE

It is the responsibility of the teacher/lecturer to ensure that employers' guidelines in relation to the COSHH regulations are complied with.

While many investigation activities may use chemicals and processes for which schools and colleges will have general assessments (which have been adopted for the purposes of risk assessment) it may be necessary in some cases to carry out a risk assessment. Employers will have guidance on such procedures. The SSERC Hazardous Chemical Manual is a source of such general assessments and Preparing COSHH Risk Assessments for Project Work in Schools published by SSERC provides advice on carrying out risk assessments.

Although teachers/lecturers are responsible for ensuring that suitable general assessments have been adopted or risk assessments have been carried out, they may wish to involve students in the risk assessment process. A simple model risk assessment form that could be used with students is included below. However, this should not be seen as a substitute for employers' procedures.

RISK ASSESSMENT FORM

Name: _____

Outline of Investigation: _____
_____
_____

Date: _____

Substance	Hazard/Risk	Strategy to reduce risk	Disposal

APPENDIX 1

The Seven Step Model

Step 1:

Do I understand all the terms used in the Investigation Brief?

Step 2:

What am I trying to discover? (What needs to be or can be investigated here?)

Step 3:

What relevant information do I already know or can I recall from my previous experience that will help me?

Step 4:

What information do I need to better understand the Brief or answer the questions I cannot answer yet?

Step 5:

Where might I get the answers I need? (What resources are available to me?)

Step 6:

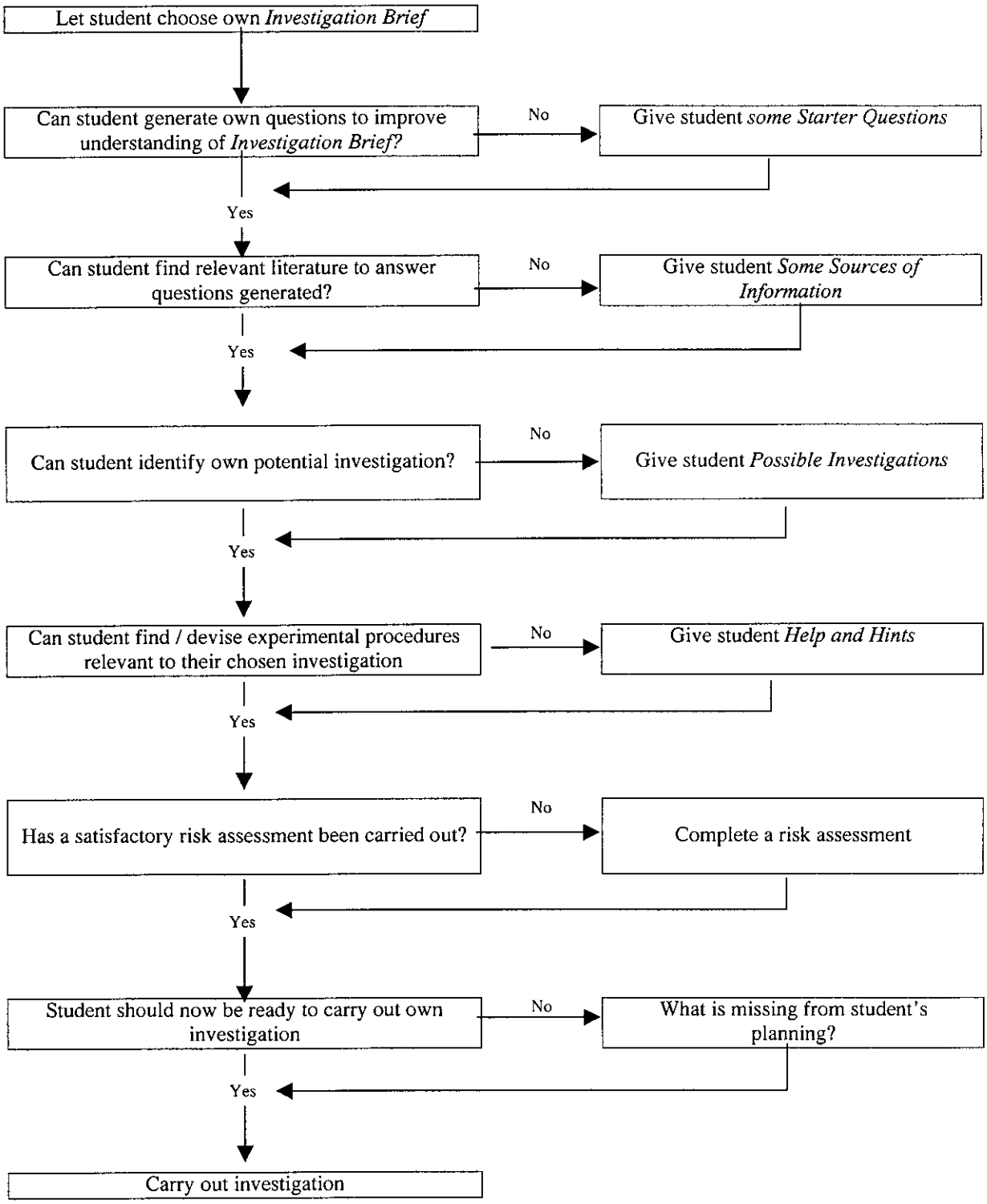
Carry out private study to find answers to the questions.

Step 7:

Having done some private study, do I now feel I have answered my questions, and can I carry out the practical work necessary to investigate what I wanted to?

APPENDIX 2

Flowchart to assist giving support to students
Teachers' Model



Aspirin

Investigation Brief

Aspirin is the most widely used drug in the world and nearly everyone will use it at some time in their lives. The earliest known uses of the drug can be traced back to ancient Greece where the physician Hippocrates used a powder extracted from willow bark to relieve pain and reduce fevers.

The real story of aspirin starts in 1897 when a German chemist called Felix Hoffman working for Bayer synthesised acetylsalicylic acid in an effort to relieve the pain suffered by his father from his arthritis. His father had, for many years, been taking sodium salicylate which was the common pain reliever at that time. Unfortunately the sodium salicylate caused severe stomach irritation and many patients could not tolerate the high doses prescribed by doctors.

Hoffman believed that acidity caused the salicylates to be severe irritants to the stomach and so he set about finding a less acidic form of the drug. It was essential that the new drug would still exhibit the therapeutic properties of the salicylates by reducing fever and inflammation while not causing as much irritation.

The name "aspirin" was given to this new drug by the Bayer chemical company and came about by the combination of "a" from acetyl, "spir" from the spirea plant which yields salicylin and "in," which is used as a common ending in medications. Aspirin soon became the pain killer of choice for physicians around the globe.

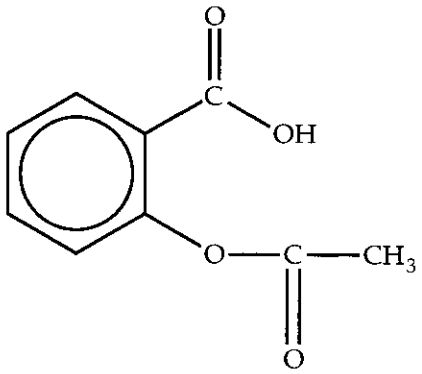
Aspirin is an **analgesic**, meaning a drug that alleviates pain without affecting consciousness. It is most commonly used for headaches, muscle pain, arthritis, and fever reduction. In 1988 the use of aspirin expanded beyond pain relief to that of a potential lifesaver. It is commonly thought that aspirin hinders prostaglandin production and thus reduces inflammation and pain. Prostaglandin affects the flow of blood platelets, which are involved in blood clotting. If plaque tears inside a coronary artery, clotting begins at the site.

Aspirin is approved as a means of reducing the risk of recurrent MI (myocardial infarction) or heart attack and preventing first MI in patients with unstable angina. It is also approved for use in the prevention of recurrent transient-ischemic attacks or "mini-strokes". In addition to its role in heart attack and stroke prevention, research continues to explore aspirin's possible role in prevention of colon, oesophageal cancer and other diseases.

In its use as an analgesic, aspirin has many alternatives. Ibuprofen is one of the most common, and is marketed under such names as Motrin IB and Advil. Ibuprofen is non-steroidal **anti-inflammatory** drug (NSAID) just as aspirin is. It has many of the same applications as aspirin.

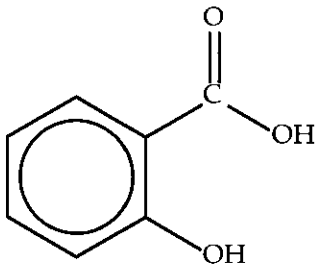
Aspirin has many side effects that ibuprofen and other pain relievers do not. It can induce gastrointestinal discomfort if taken in large enough doses. In children and adolescents aspirin can cause Reye's syndrome if taken while the child is infected with a virus like chicken pox or influenza.

The systematic name for aspirin is 2-ethanoyloxybenzenecarboxylic acid although many textbooks and papers still use the traditional name of acetylsalicylic acid.



Aspirin
(2-ethanoyloxybenzenecarboxylic acid)

Aspirin works by being hydrolysed in the small intestine to 2-hydroxybenzoic acid (salicylic acid) which is absorbed into the body.



Salicylic acid
(2-hydroxybenzoic acid)

Aspirin has also been found to act as an **anti-inflammatory, antirheumatic** and **antipyretic**. Many patients who suffer from rheumatism wear copper bracelets which they find eases their condition and it has been suggested that the salicylic acid the body produced from aspirin may be involved in helping transport copper around the body and through cell membranes by forming some type of chelated complex.

In many ways the above suggestion of salicylate acting as a ligand is similar to two cases involving iron.

i) Iron pills often contain iron(II) sulphate but unfortunately only a small proportion of the iron in the tablet is actually absorbed. Chelating the iron, using for example, Vitamin C, may speed up the movement of iron across the cell membrane and hence enhance absorption.

ii) Iron is not available to plants in alkaline soils, because it is present as insoluble iron(III) hydroxide. To make it available, it is "sequestered" i.e. the iron ion is chelated and becomes soluble even in an alkaline soil.

Some Starter Questions

- What is meant by the terms "analgesic", anti-inflammatory", "antirheumatic" and "antipyretic"?
- How is aspirin hydrolysed to salicylic acid in the body?
- What is meant by "hydrolysis"?
- How does salicylic acid bind to copper?
- What is meant by the terms "ligand", "chelate" and "chelation"?
- Why might a salicylic acid/copper complex move through cell membranes more readily than copper on its own?
- How much better is a salicylic acid/copper complex at moving through cell membranes than copper?
  Can a simulated cell membrane be set up in the lab to measure this?
- Can salicylic acid bind to other metals in a similar way?
  How do they compare to the copper complex?
- Can other organic compounds be used in place of salicylic acid to achieve the same effect?
  How does this compare to the salicylic acid/copper complex?
- What is meant by the term "sequestered"?

These are only some of the questions that could be asked. If you can think of others, please do so.

Possible Investigations

1. Patients who suffer from rheumatism wear copper bracelets which they find eases their condition. It has been suggested that the salicylic acid the body produced from aspirin may be involved in helping to transport copper around the body and through cell membranes by forming some type of chelated complex.

   Could this suggestion be true?

   - What could be used to simulate a simple cell membrane?
   - Would visking tubing, used in experiments showing the transport of glucose across a membrane, work?
   - How would you measure changes in the copper ion concentration on either side of the membrane?
   - Does the transportation process work with other transition metal ions?
   - Do any other substances act as ligands for this type of process?

2. Identification of the percentage of aspirin present in various medicines (e.g. headache tablets).

   - How could the percentage of the aspirin be found?
   - How could the aspirin be separated from the other ingredients present?
   - Would thin-layer chromatography work?

3. How does varying the concentration of aspirin or salicylic acid affect living cells?

   - What living cells could be used for this investigation?
   - Would yeast cells in a yeast culture be suitable living cells?
   - How would you observe any changes in cell structure that might occur?

4. Are aspirin substitutes as good at transporting copper across cell membranes?

   - How could a fair comparison be established?
   - How would the concentration of copper ions transported be measured?
   - What could be used to simulate a cell membrane?

This list is by no means exhaustive: there are many other possibilities which could be investigated.

Some Sources of Information

A simple procedure for both the synthesis of 2-hydroxybenzoic acid and aspirin can be found in the **Royal Society of Chemistry "Aspirin" booklet.**

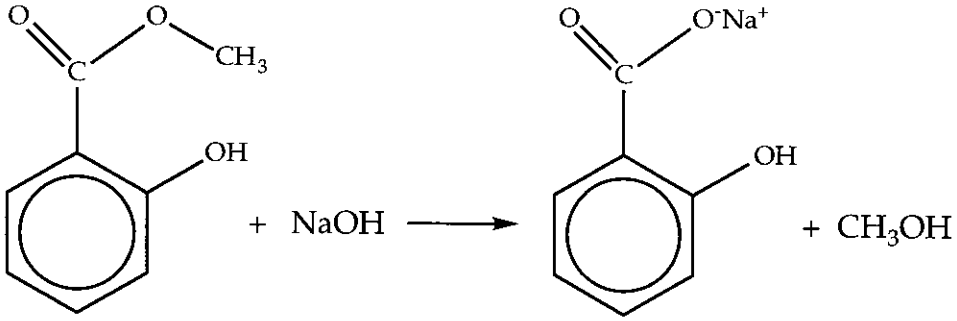
Aspirin, *Royal Society of Chemistry,* 1998, ISBN 1 870343 50 6

There are three readily available yeasts -
Bakers' yeast,
yeast used for beer making,
yeast used for wine making.

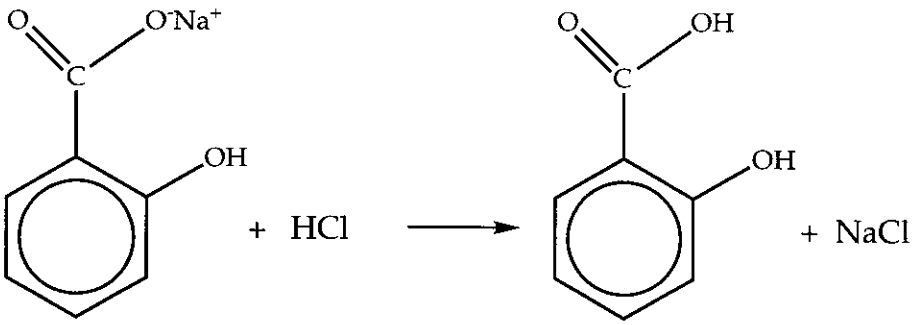
Help and Hints

Any investigation into the effectiveness and uses of aspirin could begin with synthesis of the compound. A number of activities with aspirin will already have been attempted in class in the Prescribed Practical Activities.

Most synthesis of aspirin begins with the synthesis of 2-hydroxybenzoic acid which itself can be prepared from oil of wintergreen, (~ 98% methyl 2-hydroxybenzoate).

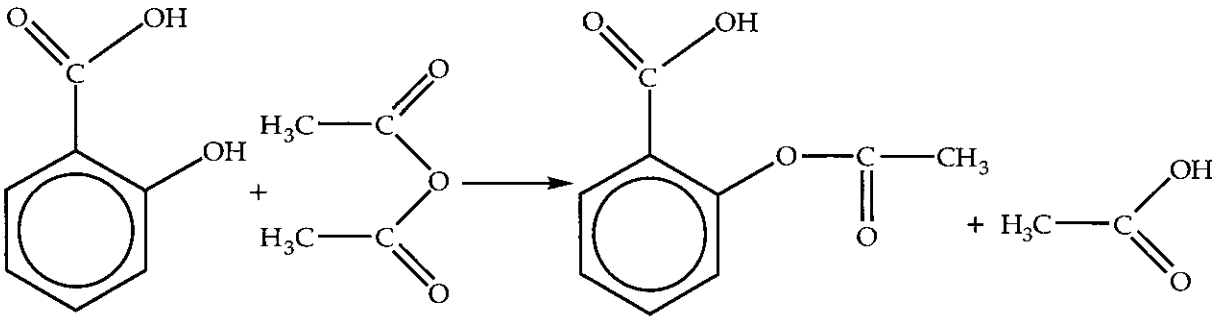


methyl 2-hydroxybenzoate



2-hydroxybenzoic acid

Once synthesised, the 2-hydroxybenzoic acid can be converted into aspirin using ethanoic anhydride.



The aspirin can then be recrystallised and the melting point of the synthesised aspirin measured to determine the purity.

Thin Layer Chromatography

For thin-layer chromatography (TLC), a glass plate, such as a microscope slide, is coated with a thin layer of very finely ground silica (SiO_2) or cellulose suspended in water or other solvent. If a spot of a solution of a compound is applied to the plate and the solvent allowed to evaporate, the compound will be adsorbed onto the surface of the plate.

If an eluent (the name given to the solvent in chromatography) of low polarity is allowed to travel along the silica coated plate, the compound has the choice of staying adsorbed or of dissolving in the eluent. If the compound is non-polar, it will dissolve and be carried along in the moving eluent. A compound in solution is being constantly exposed to fresh silica and so may be readsorbed. Equally, an adsorbed compound is being exposed to fresh eluent moving up the plate and may dissolve. Any one molecule will be constantly stepping on and off the "conveyer belt" of moving eluent. Non-polar molecules will spend most of their time in solution, and so will be carried rapidly up the plate; polar molecules will spend most of their time adsorbed, and their movement will be slow compared to the eluent. As polar and non-polar molecules move at different rates, we have a method of separating and identifying them.

Each compound can be characterised by a measurement of how far the spot has moved relative to the eluent front.

$$R_f = \frac{\text{distance moved by spot}}{\text{distance moved by eluent front}}$$

R_f values are fixed for a given compound on a given stationary phase and with a particular eluent.

Identity checks can be made using a pure sample of the compound. If the sample of pure compound and the sample of the unknown are run side by side on the same plate and they have different R_f values, then they are different compounds. If their R_f values are the same, they may be the same compound. If the eluent is changed and the two substances still have the same R_f value, it is increasingly likely that they are the same substance.

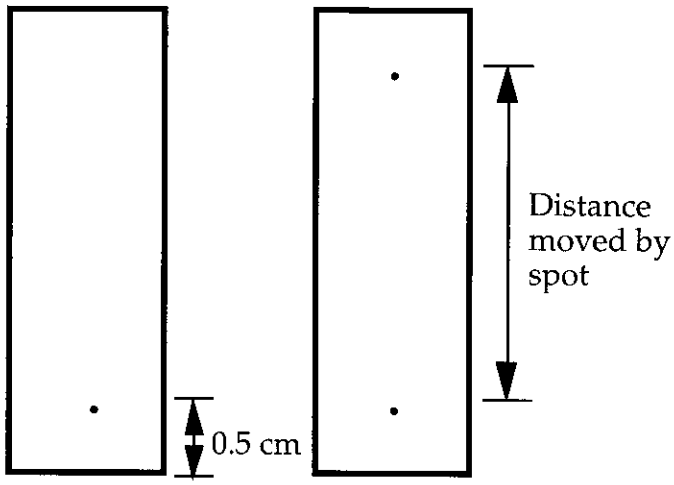
Method

Heat the middle of a capillary tube in a Bunsen flame, remove it from the flame and then pull the ends apart gently. This will cause the capillary tubing to narrow. The tube can be broken at the narrow part to give two fine tubes for making the spots on the silica plate.

Use clean microscope slides to prepare TLC plates. Put two back-to-back and dip them in a slurry of silica gel in the non-polar solvent. Carefully remove the plates, allow them to drip, and then separate them and allow to dry. Commercial alternatives are available.

Dissolve a small quantity of the compound in the solvent (or solvent mixture) being used as an eluent. Use the drawn-out capillary to spot a small amount of solution onto the plate, as indicated below. Use a separate capillary for each substance to avoid contamination.

Stand the plate in a jar containing a little eluent, taking care not to submerge the spot(s), and close the lid. Wait till the eluent has climbed up the plate, then remove the plate and allow to dry. Mark the height reached by the eluent front with a pencil or spatula.



If the compounds are coloured, R_f can measured directly. If this is not the case, the plate is exposed to some iodine crystals in a jar with the lid closed. The iodine is adsorbed where the spots are. On removing the plate from the iodine jar, the spots are marked with a pencil and the R_f value calculated.

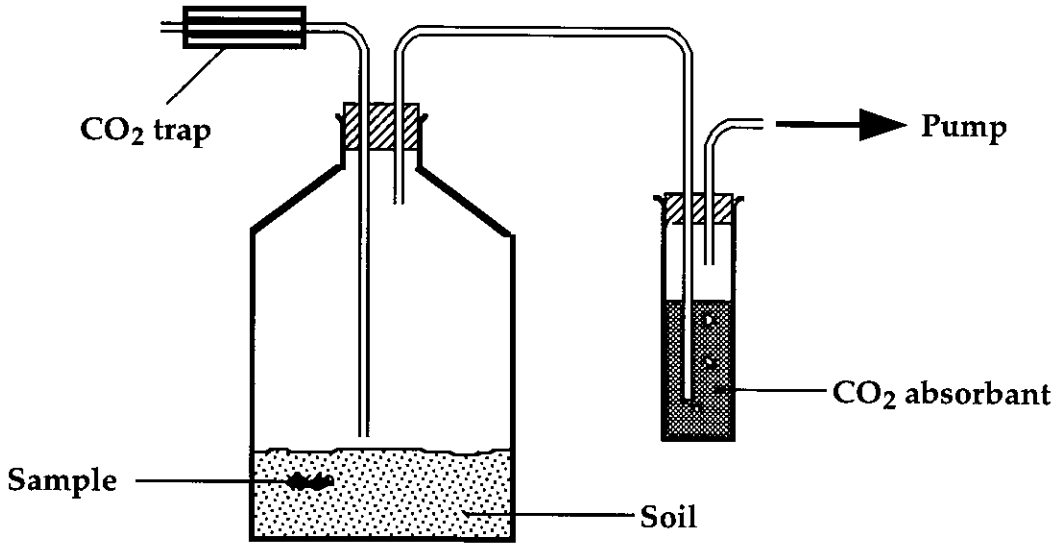
Biodegradation

Investigation Brief

Among the pollution problems of our time is the fact that many products do not decompose naturally if they are dropped or left around the countryside. The advent of plastics in the latter half of last century gave materials which were resistant to corrosion or rot. Whilst these properties often make plastics superior to natural materials, they can cause problems when plastics are disposed of. More recently there has been a move to produce plastics which have a shorter life and degrade in light or the presence of micro-organisms. One of the products of biodegradation is carbon dioxide. The production of this carbon dioxide can be used to monitor the progress of biodegradation.

One way to carry out the monitoring is in conditions as near as possible to those found in nature e.g. a material lying out or lightly buried in soil in contact with air, i.e. aerobic conditions.

A possible apparatus is shown below:



Soil is placed in a wide-necked bottle and air is drawn over it with a water pump or pond aerator. A CO_2 trap is fitted to the inlet to remove atmospheric carbon dioxide and a CO_2 absorber is placed at the outlet to collect the carbon dioxide produced. This absorber could be, for example, a known volume of sodium hydroxide solution of known concentration, but there are others which are equally good such as soda lime granules.

$$2NaOH_{(aq)} + CO_{2(g)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)}$$

It should be possible to find out after a period of time how much sodium hydroxide is unchanged or how much sodium carbonate has been formed. This needs a bit of ingenuity since both sodium carbonate and sodium hydroxide react with acid! There are several ways of surmounting this problem.

With soil only, there is bound to be some carbon dioxide produced from the biodegradation of organic material in the soil. Thus it is necessary to measure this "background" carbon dioxide before adding other weighed materials to be tested.

Note for teachers and students:
In some areas, local authorities are concerned about experiments which may be anaerobic. It is essential to keep a steady steam of air passing through the apparatus to maintain aerobic conditions. If in doubt, consult your local authority.

Some Starter Questions

- Why should the fact that plastics were resistant to rot pose a problem?
- What does "degradable" mean?
- What is the difference between "degradable" and "biodegradable"?
- Why does air have to be drawn over the soil?
- Why does atmospheric CO_2 have to be removed by the trap at the inlet?
- Explain what could be used in the trap to remove the CO_2.
- Why can sodium hydroxide be used in the absorber? What property of CO_2 does this rely on?
- Why is it essential to have a known volume and concentration of sodium hydroxide?
- What other substances could be used as the absorber?
- How could the problem that both the unreacted sodium hydroxide and the sodium carbonate formed react with acid be solved, so that only the unreacted sodium hydroxide reacts with the standard acid?
- Why is it necessary to measure the "background" CO_2 level?
- Why should the experiment be run without the sample?

These are only some of the questions that could be asked. If you can think of others, please do so.

Possible Investigations

All of these investigations use the same basic principle. There are six simple variables which can be looked at either singly or in combination. An underlying question is: "How justified are the various claims made by supermarkets that their 'green' plastics are biodegradable?"

1. Do different soil types e.g. loam, sand, clay etc., affect the biodegradation of samples? What about an alkaline soil, found in limestone/ chalk areas?

2. Does temperature affect the biodegradation of samples?

3. Does the fact that the sample is exposed to light or is kept in the dark affect the biodegradation?

4. Does the type of polymer in the sample chosen affect the biodegradation?

   Do naturally occurring organic substances like apples biodegrade faster than man-made biodegradable polymers?

5. Does the dampness of the soil affect the biodegradation?

6. How does the length of time the sample is left to degrade affect the biodegradation?

   - Which type of polymers break down the fastest?
   - Are the new man-made substances "better" at decomposing than nature's own?
   - What are the problems associated with slow biodegradation?

This list is by no means exhaustive: there are many other possibilities which could be investigated.

Some Sources of Information

Recent Polymers - Support Notes for Higher Chemistry, *SCCC*, 1999
ISBN 1 85955 836 4

General Information on Biodegradation might be found on the Green Chemistry Network
http://www.chemsoc.org/networks/gcn/

Help and Hints

One problem to overcome when trying to calculate how much carbon dioxide has been released is that both sodium carbonate and sodium hydroxide react with acid. This idea might at first seem difficult, but a little thought and recall of some basic chemistry will help. A carefully selected dual indicator titration could be carried out or a pH meter linked to a data-logging device could be used.

The sodium carbonate formed in the reaction is soluble and alkaline and, like the sodium hydroxide, will react with a standard solution of hydrochloric acid.

$$2NaOH_{(aq)} + CO_{2(g)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \qquad \text{Equation } 1a$$

An alternative is:

$$NaOH_{(aq)} + CO_{2(g)} \longrightarrow NaHCO_{3(aq)} \qquad \text{Equation } 1b$$

Another way to overcome the problem is to add some barium chloride ($BaCl_2$) solution to the mixture. This reacts to form the insoluble white precipitate, barium carbonate ($BaCO_3$) which can then be filtered off. The other product is the neutral salt, sodium chloride which is soluble and will not react with the standard acid solution.

$$Na_2CO_{3(aq)} + BaCl_{2(aq)} \longrightarrow BaCO_{3(s)} + NaCl_{(aq)} \qquad \text{Equation } 2$$

Yet another method is possible and involves weighing the barium carbonate produced in reaction shown by equation *2*. This allows the number of moles of sodium carbonate produced in reaction *1a* or *1b* to be calculated, and hence, the number of moles of sodium hydroxide which have reacted in the initial reaction.

With the sodium carbonate, as barium carbonate, removed it is now possible to carry out a titration between the unreacted sodium hydroxide and the standard hydrochloric acid solution. This allows the number of moles of unreacted sodium hydroxide to be calculated.

$$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)} \qquad \text{Equation } 3$$

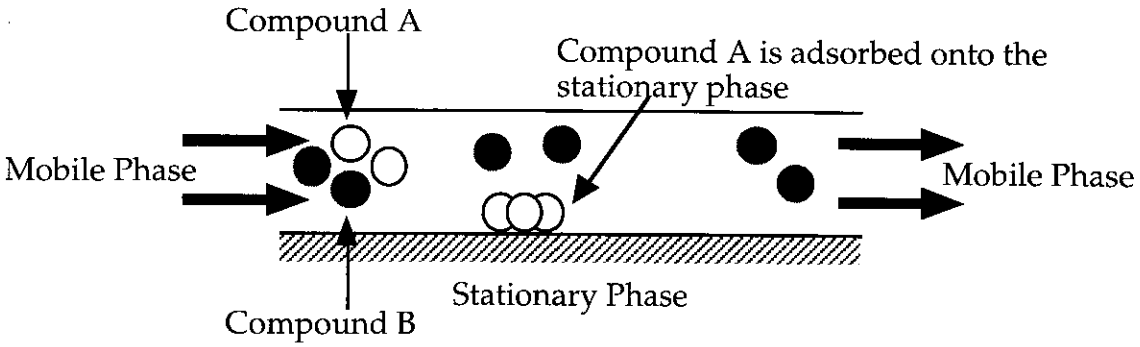
Depending on which experiments are carried out determine the form of the calculation. In each case the number of moles of sodium hydroxide present at the start is required.

Chromatography

Investigation Brief

Chromatography is a process which can be used to separate compounds based on their ability to bind to a stationary phase or a mobile phase. This can be used to separate a mixture of compounds or even to identify a compound by comparing it with a sample of known identity. There are many different kinds of chromatography, but they all work in essentially the same way.

In chromatography there is a stationary phase (e.g paper or silica gel) and a mobile phase (a liquid or gas). The mixture of compounds to be separated is carried in the mobile phase where it interacts with the stationary phase. Each component of the mixture interacts differently with the stationary and mobile phases, due to that component's ability to bind to either phase, with the result that each component moves at a different rate over the stationary phase, giving a separation.



A compound in solution is being constantly exposed to fresh stationary phase and so may be adsorbed onto the stationary phase. Equally, an adsorbed compound is being exposed to fresh mobile phase and may dissolve. Any one molecule will be constantly stepping on and off the "conveyer belt" of the mobile phase. Molecules which spend most of their time in solution will be carried rapidly over the stationary phase and move further; molecules which spend most of their time adsorbed onto the stationary phase will not move as far.

Different types of chromatography are possible depending on the choice of stationary phase and mobile phase (which is called an eluent - the name given to a solvent in chromatography).

Paper chromatography uses paper sheets as the stationary phase, and an eluent is allowed to move over the paper carrying compounds with it.

Thin layer chromatography (TLC) is very similar, except that glass plates coated with a layer of damp silica (SiO_2) or cellulose are used. A spot of a solution of a compound is applied to the plate. The solvent is allowed to evaporate and the compound will remain adsorbed onto the surface of the plate.

The plate is then placed in a jar containing a little eluent, taking care not to submerge the spot, and the lid closed. As the eluent climbs up the plate, the compound will be carried up the plate too. When the plate is removed from the jar the level the eluent travelled can be marked.

Each compound can be characterised by a measurement of how far the spot has moved relative to the eluent front, called an R_f value:

$$R_f = \frac{\text{distance moved by spot}}{\text{distance moved by eluent front}}$$

R_f values are fixed for a given compound on a given stationary phase and with a particular eluent.

Identity checks are made using a pure sample of what we think the compound is. If the sample of pure compound and the sample of an unknown are run side by side on the same plate and they have different R_f values, then they are different compounds. If their R_f values are the same, they may be the same compound. If the eluent is changed and the two substances still have the same R_f value, it is increasingly likely that they are the same substance.

If the compounds are coloured, R_f can measured directly. If this is not the case, the plate is exposed to some iodine crystals in a jar with the lid closed. The iodine is adsorbed where the spots are. On removing the plate from the iodine jar, the spots are marked with a pencil and the R_f value calculated.

"Flash chromatography" is a way of separating different compounds using silica as the stationary phase. The silica is packed into a sinter funnel and the eluent is washed through under vacuum into a Buchner flask. If a mixture of compounds is washed through the silica with a non-polar solvent the polar compounds will remain adsorbed onto the silica. Further washings with increasingly polar eluents will remove compounds from the silica in order of increasing polarity. This method allows larger quantities of substance to be dealt with compared with paper or thin-layer chromatography.

Gases can also be separated/ identified by chromatography, called GLC (Gas Liquid Chromatography). Detergent powder packed into a very long glass tube can be used as a stationary phase, and ordinary gas from a gas tap (which is essentially methane, CH_4) used as the mobile phase. If the carrier gas is set alight, changes in the flame, such as colour, temperature and electrical conductivity, caused by different components passing through the tube can be detected.

This is done by introducing a mixtures of gases via a rubber cap (septum) with a hypodermic syringe and the time taken for them to pass through the column measured. With compounds of similar polarity such as hydrocarbon mixtures, the size (length and shape) of the molecule determines the time taken to pass through the column - other things being equal, smaller molecules pass through more quickly.

Some Starter Questions

- What is meant by "ability to bind to a stationary phase or a mobile phase"? How does this work in different kinds of chromatography?
- What does "adsorbed" mean?
- Do different kinds of paper give different separations of compounds?
- What is paper made of? How might it act to separate the molecules?
- What kind of compounds would be best separated on silica coated plates? What kind of compounds would be best separated on cellulose coated plates?
- Does the length of the stationary phase matter in the different types of chromatography? Do longer TLC plates or GLC tubes, or sinter funnels in flash chromatography, give better separation than shorter ones?
- How do detergent powders act as stationary phases? Do different detergent powders act equally well? What are detergent powders made of?
- Why do different compounds burn differently? Why do flame colours change?
- How can changes in a flame's temperature or conductivity be measured? What sort of equipment is needed?
- Many materials are made up of mixtures. How many components are present in a particular mixture? How could these components be identified?
- How sensitive are the different techniques of separating compounds? Can different compounds with the same functional group be separated easily?

These are only some of the questions that could be asked. If you can think of others, please do so.

Possible Investigations

Paper/ Thin Layer Chromatography

1. Compare paper, TLC (silica), TLC (cellulose) for their ability to separate a variety of compounds.

   Possible compounds for investigation: carbohydrates,
   amino acids,
   transition metals.

Gas Chromatography

2. What is the best detergent powder for separation?

3. Does the temperature of the tube affect separation?
   Try putting the tube in a heated box or a water bath.

4. What detector system could be used to detect temperature changes in the flame?

   - Could flame height be used to detect different materials?
   - What compounds give different flame colours?
   - Could a thermocouple be used?

5. What hydrocarbons are present in lighter fuel or bottled gas?
   How many are there?

   To identify components of a mixture, pure samples have to be used and their exit times recorded. The mixture will then give a number of responses at times corresponding to those of the pure substances.

This list is by no means exhaustive: there are many other possibilities which could be undertaken.

Some Sources of Information

Relevant manuals for various commercial TLC/ paper chromatography/ GLC apparatuses.

"Polarity and Selectivity of Ionic Stationary Phases Used in Gas Chromatography: Evaluation of Commercial Detergents Containing Anionic Surfactants as Column Packing" by K.G. Furton & A. Mantilla, *Journal of Chemical Education*, 1991, **68**, 74

Help and Hints

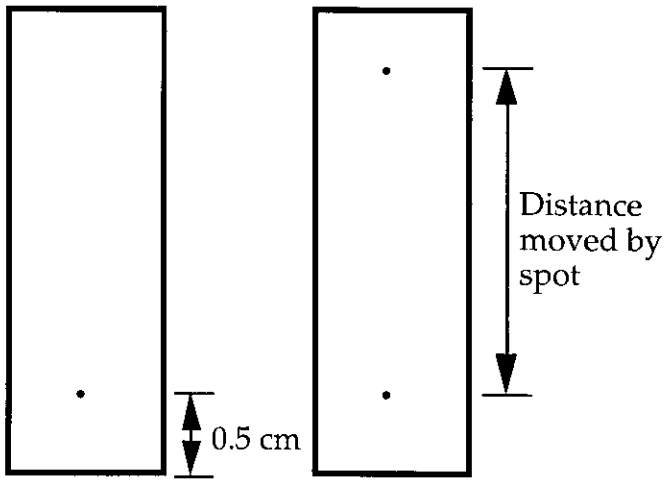
Thin Layer Chromatography

Heat the middle of a capillary tube in a Bunsen flame, remove it from the flame and then pull the ends apart gently. This will cause the capillary tubing to narrow. The tube can be broken at the narrow part to give two fine tubes for making the spots on the silica plate.

Use clean microscope slides to prepare TLC plates. Put two back-to-back and dip them in a slurry of silica gel in the non-polar solvent. Carefully remove the plates, allow them to drip, and then separate them and allow to dry. Commercial alternatives are available.

Dissolve a small quantity of the compound in the solvent (or solvent mixture) being used as an eluent. Use the drawn-out capillary to spot a small amount of solution onto the plate, as indicated below. Use a separate capillary for each substance to avoid contamination.

Stand the plate in a jar containing a little eluent, taking care not to submerge the spot(s), and close the lid. Wait till the eluent has climbed up the plate, then remove the plate and allow to dry. Mark the height reached by the eluent front with a pencil or spatula.



If the compounds are coloured, R_f can measured directly. If this is not the case, the plate is exposed to some iodine crystals in a jar with the lid closed. The iodine is adsorbed where the spots are. On removing the plate from the iodine jar, the spots are marked with a pencil. The R_f values can then be calculated.

Flash Chromatography

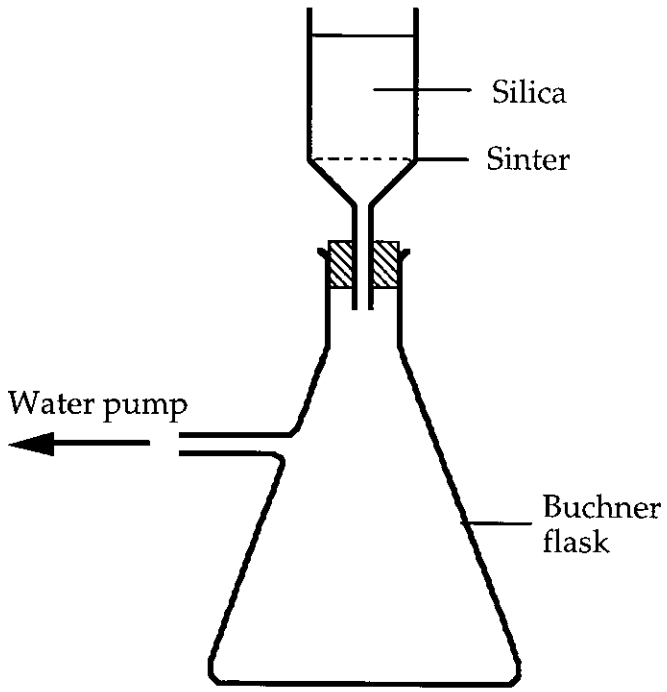
A Buchner flask, fitted with a sintered glass funnel (try a normal Buchner flask with a filter paper over the holes) is attached to a water pump. A slurry of silica in a non-polar solvent is poured into the funnel to form a layer at least 5 cm deep. Turn on the pump and draw the solvent through slowly to leave an even layer of silica, and continue to draw air through until the silica layer is dry. If it shows signs of channelling, start again!

Pour carefully and evenly on top of the silica the solution of the mixture to separated, dissolved in the least polar solvent.

Apply the vacuum and wash the silica through with this least polar solvent to elute the least polar compound in the mixture. Then draw air through the silica to dry it. Empty the Buchner flask, or replace it with another, and then continue the elution, this time with a slightly more polar solvent. Collect the component, dry the silica bed and then repeat the process with a succession of solvents, in the order of increasing polarity, until the final component is washed off the silica. If the mixture contains coloured materials the separation will be clearly visible.

Solvents such as pentane, hexane, ethyl ethanoate and methanol should be adequate for most separations.

NB ***Dangers arising from the flammability of these solvents***



Gas Chromatography

A simple version of this technique can be operated in schools.

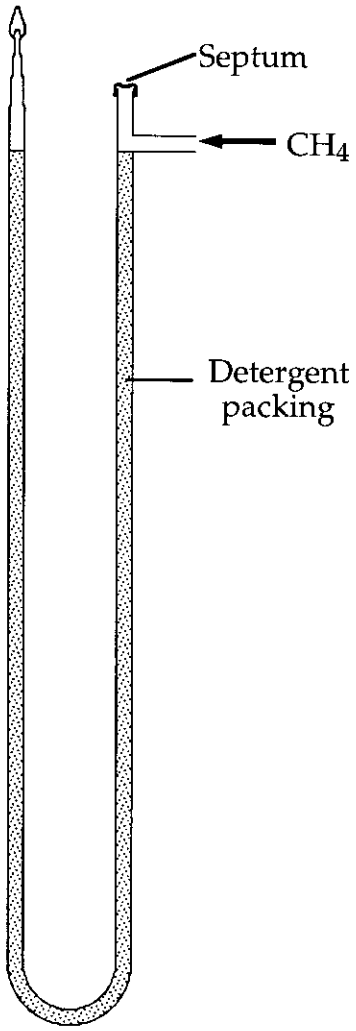
At least a metre of glass tubing should be bent into a U-shape and carefully filled with a detergent powder a little at a time. The packing of the tube is important so that it is not so tight that gas cannot get through it, but also it should have no gaps or vacant channels. The packing should be done by adding a few grams of powder at a time and tapping gently on the outside of the tube to make the powder settle evenly. The tube should be almost completely filled to cut out any "dead space", that is space which is empty and in which no separation will take place.

One limb is fitted with a small T-piece and the other with a glass jet (or even a hypodermic needle). The T-piece is used to introduce the carrier gas (ordinary gas from the tap) and also as a port for injecting the mixture to be separated, This is best done with a rubber cap (septum) through which the mixture can be injected with a hypodermic syringe.

At the outlet of the U-tube the jet is used to burn the gas. As the components of the mixture come through they alter the methane flame in a number of ways: its colour, its height, its temperature, its electrical conductivity.

N.B. The jet must not be lit before some precautions are taken. To begin with the gas spaces in the tube are filled with air. As the air is being displaced by the methane gas, mixtures of air and methane will come out of the jet and such mixtures can be explosive. Sit a very small test tube over the jet for a minute or so, and then take it to a flame and light the contents. If they light with a pop, repeat the process until the tube's contents burn quietly.

Then light the jet. Some sort of draught protection will be needed round the flame to keep it steady.



A thermocouple hooked up to a computer is one possible way of measuring changes in the flame.

If organic materials containing halogen atoms are being separated, they can be detected by placing a coil of copper wire in the flame. The flame will be pale blue for the carrier gas, but will give a green colour when halogen compounds come through.

Continuous Variation

Investigation Brief

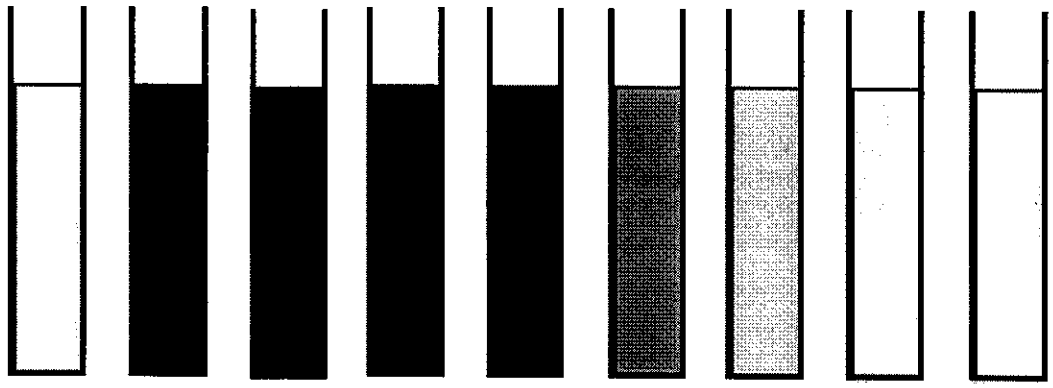
When two substances react to form a product there will be an optimum mole ratio value of the starting substances to produce maximum yield of the product. For example, the production of water from an acid and a base will be at its maximum when the acid and base just neutralise each other. If both reactants are monobasic, this will occur at a 1:1 mole ratio, but if the acid is dibasic, the best ratio will be 1:2.

In many reactions, the composition of the product may be unknown. By varying the mole ratios of the reactants until maximum product is achieved, information about the composition of the product is obtained. For example, the composition of many transition metal complexes cannot be predicted in advance of their synthesis and has to be determined experimentally. This effect could be used to show the type of ligands or the oxidation state of the metal involved.

But how can we know when the maximum yield has occurred? The most convenient way is to use some physical property which can be monitored and which will attain a maximum (or a minimum) at the point of maximum yield of product.

Perhaps the simplest way to approach this is by the method of continuous variation which is shown below.

Let A and B represent the reactants. Nine test tubes are made up as follows-



A	9	8	7	6	5	4	3	2	1
B	1	2	3	4	5	6	7	8	9

Volumes in cm^3

Some physical property is measured for each such as:

1. Colour (absorbance) if a coloured compound is formed.

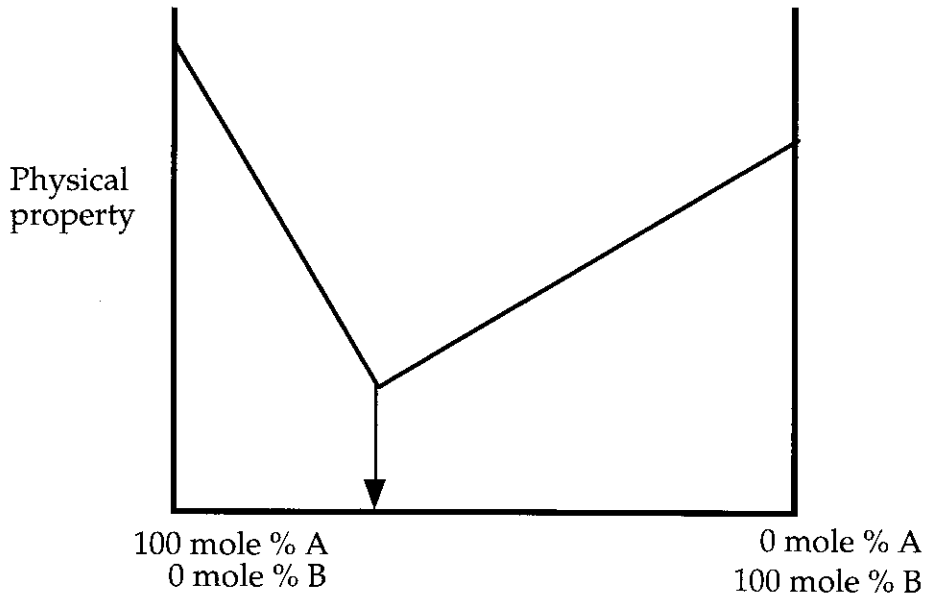
2. Conductance if ionic substances are involved.

3. pH.

4. Temperature change (in this case measurement would have to be made immediately after each tube was mixed).

5. Amount of precipitate if a solid product is formed. e.g. depth of precipitate, mass of precipitate after filtration.

A plot of readings against mixture compositions can give maxima or minima.



The product is therefore formed by two moles of A and one of B. If the product is an adduct, it would have the formula A_2B.

Some Starter Questions

- What is a "mole ratio"?
- What is meant by an "optimum" mole ratio?
- What is meant by "monobasic" and "dibasic" acids?
- What is meant by a "transition metal complex"?
- What substances form complexes with transition metals?
- What is a "ligand"? What types of ligands can be used?
- What type of ions are coloured?
- What is meant by the term "oxidation state"?
- What is meant by "equimolar"?
- How could the colour of a compound be detected?
- How could the intensity of the colour of a compound be measured?
- How could the conductivity of a compound be measured?
- How could the pH of a compound be measured?
- How could the temperature change in a reaction be measured accurately?
- How could the amount of precipitate be measured accurately?
- What is an "adduct"?

These are only some of the questions that could be asked. If you can think of others, please do so.

Possible Investigations

Any investigation undertaken is dependent on the choice of A and B.

1. A and B can be acids and bases.

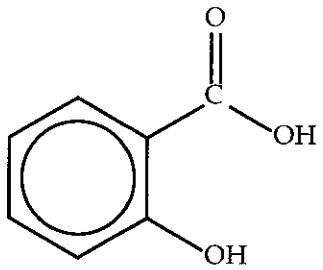
   If one is coloured so that indicators would be ineffective, temperature changes can be monitored because $H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$ is exothermic.

2. Metal ions and ligands forming a coloured solution.

   Ligands can be the normal inorganic ones or amino acids, amines etc. and the metal ion centres can be from the transition metal range with varying oxidation states.

   Do complexes form and if so, what is their formula?

3. It has been suggested that salicylic acid, produced in the body from aspirin, may be involved in the transport of copper around the human body.



Salicylic acid
(2-hydroxybenzoic acid)

   Some arthritis sufferers wear copper bracelets to ease their condition.

   Using the method of continuous variation, an investigation can be carried out to see if there is any evidence that copper forms a complex with aspirin which would allow it to pass through cell membranes. Copper cannot do this on its own as it is not soluble in the materials cell membranes are made of.

Having decided the system, decide upon the appropriate physical property to be measured and the concentrations which will make this detectable. Low concentrations may make temperature changes difficult to measure whereas high concentrations may make colours too dark.

This list is by no means exhaustive: there are many other possibilities which could be investigated.

Crystals

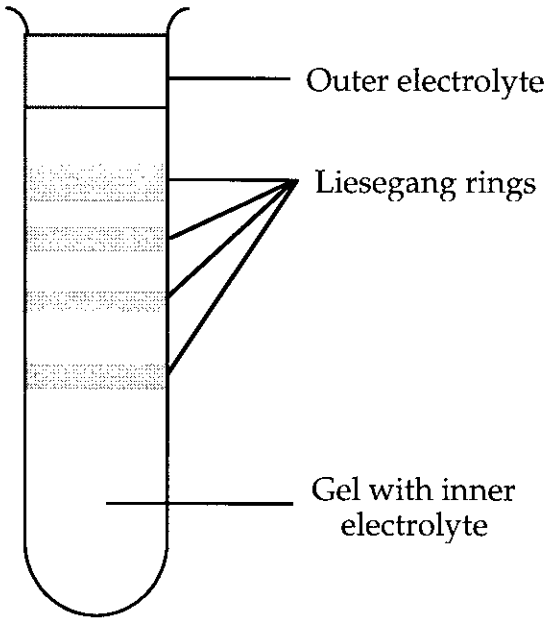
Investigation Brief

Crystal growth has long been an area of considerable research in chemistry. Primarily, this is because advances in solid state science often hinge on the availability of single crystal specimens. Furthermore, the intrinsic beauty of crystals, including gel grown crystals, has made their growth desirable for many.

One of the simplest methods for growing crystals in gels is to use the "diffusion technique". This involves dissolving an electrolyte, the so-called inner electrolyte, in a gel solution and allowing the gel to set. Once the gel has set a solution of a second electrolyte, called the outer electrolyte, is poured onto the gel surface. A reaction is observed as the outer electrolyte diffuses through the macromolecular structure of the gel and, within two or three weeks, crystals of up to a centimetre in length can start to form. **Completion of the reaction requires approximately one month.**

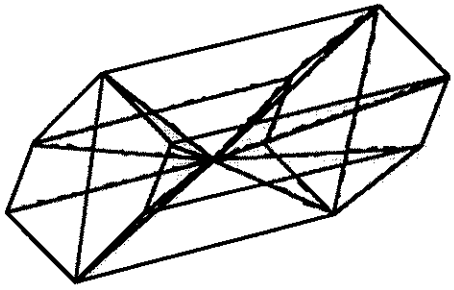
It is essential to choose appropriate electrolytes. Both should be water soluble, but only one of the products of the reaction should be insoluble. For example:

$$Pb(NO_3)_{2(aq)} + KI_{(aq)} \longrightarrow PbI_{2(s)} + KNO_{3(aq)}$$

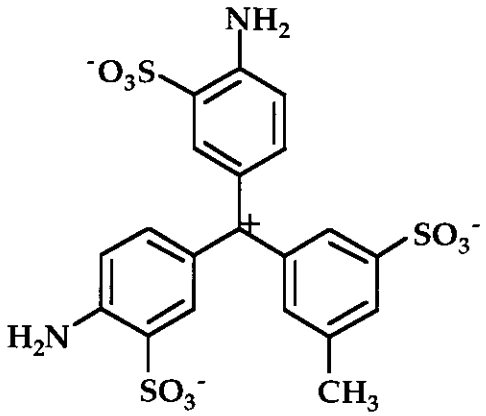


When the diffusion technique is utilised it is often found that crystals grow in banded arrangements known as "Liesegang Rings" after the German colloid chemist, Dr Raphael Liesegang, who first observed the phenomenon in 1896. Rings of this kind are observed in nature in minerals such as malachite and banded agate. Liesegang rings are an example of "a chemical reaction which oscillates in time and space." The reaction of millions of moving molecules organising themselves into patterns in time and space are what make the study of this phenomenon so interesting. These rings have perplexed chemists since they were discovered and the reasons for their formation are still not fully understood. However, a great many factors influencing their formation have been identified and are open to practical investigation.

In other studies simple salt crystals have been found to incorporate organic dyes into particular faces producing a 'bow-tie' effect. These crystals have been called *organic hourglass inclusions* (HIs). This unusual phenomenon is caused by large organic molecules being included in simple ionic lattices. This type of crystal was first observed by de Sénarmont in 1854 while growing $Sr(NO_3)_2.4H_2O$ in a water solution containing a red dye which was found in children's chemistry sets of the day.



This effect is shown by potassium sulphate (K_2SO_4) crystals grown in the presence of the dye, acid fuchsin. The dye is not absorbed uniformly throughout the crystal and produces crystals with the characteristic 'bow-tie' structure.



Acid fuschin

This particular HI system was discovered by Harold Buckley in the 1930's and is probably the easiest one to investigate.

Some Starter Questions

- What is meant by a "diffusion technique"?
- How will the type of solution affect the formation of Liesegang rings?
- Might the pH of the solution affect the formation of Liesegang rings? Might there be an optimum pH for the formation of Liesegang rings?
- How might passing a current through the gel affect the formation of Liesegang rings?
- Will the type of electrodes used affect the formation of Liesegang rings?
- Will using an AC or DC current affect the formation of Liesegang rings?
- Does the type of vessel the gels are grown in affect the formation of rings?
- Does changing the outer electrolyte during the experiment alter the formation of Liesegang rings?
- What factors will affect the formation of organic HIs?
- Does the choice of the original salt matter?
- Does temperature affect the crystal growth in dyes or in gels?
- Are there different faces in a crystal?
- Does the dye only go into certain faces?
- Do different dyes go into different faces or planes?

These are only some of the questions that could be asked. If you can think of others, please do so.

Possible Investigations

There are innumerable factors which influence crystal growth in gels, any one of which could form the basis of an investigation.

1. What effect does varying the concentration of reactants have on the crystal size, colour, shape etc.?

   - What is the effect of varying the pH?
   - Is there an optimum pH for crystal growth?
   - Compare two test tubes, one containing sodium silicate gel, the other gelatin with all other conditions being the same.
   - If the test tube is half filled with sodium silicate gel, half with gelatine, does this affect the growth of the crystals?

2. What is the effect of passing an electric current through the gel?

   - Do the crystals grow in any particular pattern?
   - Is there a difference when an alternating current is used rather than direct current ?

3. When Liesegang rings are grown is there any difference in the size, shape, or colour of the crystals in each ring?
   (The most effective way of investigating such things may be to cut off the bottom of the test tube, extrude the gel cylinder, slice the gel along each ring and look at the crystals under a hand lens or microscope).

4. If the type of vessel used to grow the crystals is changed from a test tube to a conical flask, say, do Liesegang rings still grow?

   - If so, how are they affected?
   - What happens when the outer electrolyte is changed half way through the reaction?
   - Are any differences observed if the 'inner electrolyte' and the 'outer electrolyte' are interchanged?

5. Use an inner electrolyte containing ions of a metal low in the activity series. Place on the surface of the gel a plate of a metal higher in the activity series. Crystals of the less active metal should be produced. Are they? Where?

6. Varying concentration and choice of dye to exhibit different properties.

7. Changing the crystal type to look for differences in crystal structure.

8. Seeing what effects concentration, temperature, length of growing time etc. have on crystals and the uptake of dye.

9. Growing large crystals - the best crystals are not formed by evaporation but by cooling a warm saturated solution slowly. A saturated solution is prepared at a temperature higher than room temperature. This is allowed to cool slowly, e.g. in a vacuum flask.

   Another good method for growing large crystals involves placing a beaker of a saturated solution in a thermostatically controlled water bath and suspending a seed crystal in it. If the solution is allowed to evaporate slowly good, regular shaped crystals will form.

This list is by no means exhaustive: there are many other possibilities which could be investigated.

Some Sources of Information

For Liesegang Rings and Growth in Gels

"An Interesting Student Chemistry Project: Investigating Liesegang Rings" by R. A. Schibeci and C. Carlsen, *Journal of Chemical Education*, 1988, **65**, 365;

"An Experimantal Study of Liesegang Phenomenon and Crystal Growth in Silica Gels" by A. H. Sharbaugh III and A. H. Sharbaugh Jr., *Journal of Chemical Education*, 1989, **66**, 589;

"Crystal Growth in Gels" by S. L. Suib, *Journal of Chemical Education*, 1985, **62**, 81;

"Crystals In Gels and Liesegang Rings" by H. K. Henisch, *Cambridge University Press*, Cambridge, 1988.

For Crystal Growth in Dyes

"Organic Hourglass Inclusions" by B.Kahr, J.K.Chow and M.L.Peterson, *Journal of Chemical Education*, 1994, **71**, 585

Help and Hints

A. *Liesegang Rings*

For examples of the types of crystals and Liesegang rings which can be grown, and instructions on which electrolytes to use, see Some Sources of Information.

Method

The following is a standard method for growing crystals in gels and should be used in conjunction with the sources of information given.

1. A standard gel solution should be made. This can be done by making up a solution of sodium silicate of density 1.06g cm^{-3}. Alternatively, the gel can be made by following the instructions on a packet of gelatin. (The sodium silicate solution can give better results, but only if it is absolutely free from pollutants such as CO_2, so don't use any that has been lying around for a long time).

2. Add the inner electrolyte to 15 cm^3 of the gel solution and then add this to 15 cm^3 of 1mol l^{-1} acetic acid (this is not necessary when gelatin is used). This should be done dropwise with constant stirring so as to prevent excessive local ion concentration which would result in the formation of turbid gels. Allow the gel to set in a test tube or some other vessel of your choice.

3. Once the gel has set, carefully pour a few cm^3 of the second electrolyte on to the gel surface and cork the test tube.

4. Leave the gel for a period of weeks.

Systems which have produced Liesegang rings within two weeks

R. A. Schibeci and C. Carlsen, *Journal of Chemical Education*, 1988, **65**, 365

Gel containing	Solution on top
cobalt(II) chloride	concentrated("0.880") ammonia
magnesium chloride	sodium hydroxide (19 mol l^{-1})
magnesium chloride	concentrated ammonia
copper(II) sulphate	silver nitrate solution (0.1 mol l^{-1})
manganese(II) chloride	concentrated("0.880") ammonia
copper(II) chloride	sodium hydroxide (19 mol l^{-1})
potassium chromate	silver nitrate solution (0.1 mol l^{-1})

B. ***Crystal Growth in Dyes***

The following method can be used for growing organic hourglass inclusions (HIs)

Method

1. About 20 g of K_2SO_4 is dissolved in 200 cm^3 of distilled water.

2. The dye solution is 30 mg of acid fuchsin (sodium salt) dissolved in 30 cm^3 of water.

3. 60 cm^3 of the K_2SO_4 solution is placed in each of three petri dishes to which 4, 8, and 12 cm^3 of the dye solution is added.

4. The dishes are left for a week or so on the bench after which time the best formed crystals are selected and examined. Are there any bow-ties?

CAUTION: treat acid fuchsin with care and as with most dyes, avoid contact with the skin and avoid inhalation. The solid can be an irritant and should be handled only with gloves in a fume hood.

It is possible to use other dyes and different starting solutions. A table of dyes and crystals, as well as the plane in which they grow, is given below.

A selection of dyes and host salts which can produce HI's

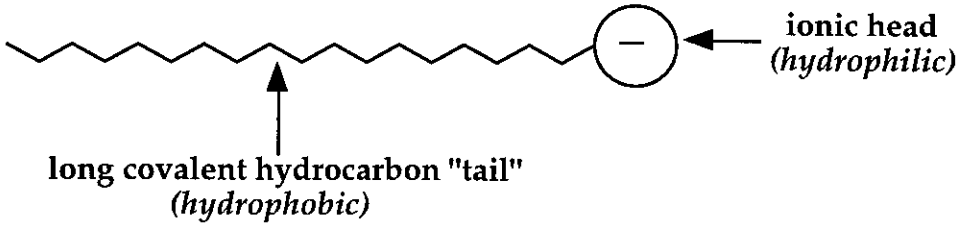
B.Kahr, J.K.Chow and M.L.Peterson, *Journal of Chemical Education*, 1994, **71**, 585

Dye	**Host Salt**
Methylene blue	$Ba(NO_3)_2$
Methylene blue	$Pb(NO_3)_2$
Naphthol green	K_2SO_4
Acid fuschin	K_2SO_4
Acid fuschin	K_2SeO_4
Quinoline yellow	K_2SO_4
Quinoline yellow	NH_4ClO_4
Amaranth	K_2SO_4
Amaranth	$KAl(SO_4)_2 \cdot 12H_2O$

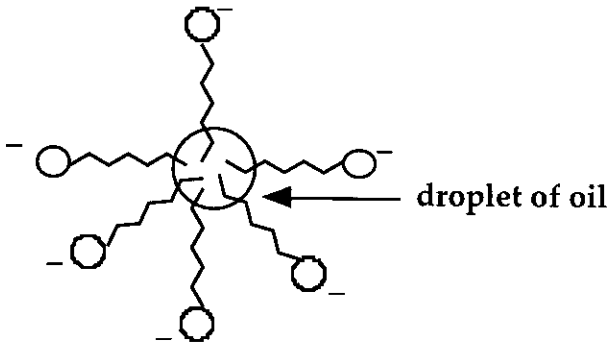
Detergents

Investigation Brief

Substances which make good cleaning agents have, in their molecules, a water hating (hydrophobic) part which dissolves in oils and fatty materials, and a water liking (hydrophilic) part. The hydrophobic part is generally a long hydrocarbon chain with 10-20 carbon atoms in it, while the hydrophilic part is charged in some way (ionic properties) or can form hydrogen bonds with water.



The cleaning action takes place when the molecules force their hydrophobic tails into the oily medium leaving their hydrophilic heads sticking out of the surface of the oil drop so that the drop has a charged or hydrogen bonding surface. These surface charged droplets are called **micelles;** they all have the same charge and so repel one another and remain in suspension in the water as an emulsion or colloid.



There are four categories of surfactant each with its own behaviour and uses. How they interact with one another is also important.

Car drivers may be familiar with an effect of mixing two different kinds of surfactant. Water in car windscreen washer systems often has a detergent added to help the cleaning action. Sometimes the system will stop working even though the reservoir has water in it, and further examination of the system will reveal the water jets blocked by a jelly-like substance. The substance is formed when two different kinds of surfactants are mixed - the driver may have switched the brand of detergent used in the system or have topped up the system with water from a garage using a different detergent.

Another common example of the effect of mixing detergents is observed when the bubbles from a bubble bath come into contact with a bar of soap. The bubbles burst because the soap and the bubble bath contain different types of surfactants.

Types of surfactant molecules

- Anionic surfactants carry a negative charge
  e.g. $C_{17}H_{35}COO^- Na^+$
  Soap is an example of this type of surfactant and anionic surfactants are also used in shampoos because they have very good cleansing and foaming properties.

- Cationic surfactants carry a positive charge
  e.g. $(C_{18}H_{37})_2 N (CH_3)_2^+ Cl^-$
  This is like ammonium chloride ($NH_4^+ Cl^-$) with the hydrogen atoms replaced by alkyl groups (octadecyl and methyl in this example). This type of surfactant is used most commonly in fabric conditioners and also as a cleaning agent and disinfectant in the kitchens of hospitals and restaurants. Contact with the skin can cause severe irritation.

- Non-ionic surfactants carry no charge and depend upon hydrogen bonds from the OH group and the ethylene oxide units being made to water.
  e.g. $C_{15}H_{31} (OC_2H_4)_7 OH$
  This type of surfactant is usually used to modify the effect of the main surfactant in a detergent. They tend to be used as emulsifiers or foam modifiers.

- Amphoteric surfactants have both positive and negative charges in their molecules.
  e.g. $C_{12}H_{25} N^+ (CH_3)_2 CH_2CO_2^-$
  This type of surfactant is extremely pH dependent. At a very low pH it will exhibit properties of a cationic surfactant whereas at high pH it will behave like an anionic surfactant. Due to the fact that these surfactants are low foaming and have little irritability to the skin they tend to be used in baby care products.

Some Starter Questions

- Why is the long hydrocarbon chain hydrophobic?
- Why do micelles form in the way they do?
- What is an "emulsion"?
- What is a "colloid"?
- How do an emulsion and a colloid differ?
- What does "amphoteric" mean?
- How might the amphoteric properties be important here?
- Would pH changes affect the charge on a surfactant molecule?
- How can two foam-creating substances "cancel each other out"?
- How would the concentration of the detergent affect its properties?
- How might temperature affect the detergency action?
- Explain whether the type of water (hard or soft) affects the detergent?
- Are all types of surfactants used commercially?
- How could the type of surfactant present in a detergent be identified?

These are only some of the questions that could be asked. If you can think of others, please do so.

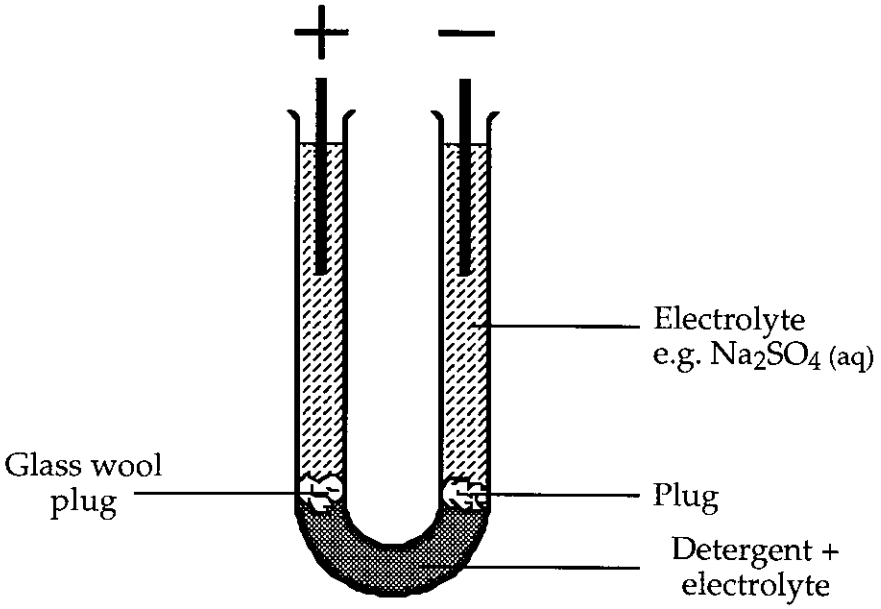
Possible Investigations

In this section a number of the suggestions could be used together to produce an effective investigation.

1. Using surfactants in pairs, try to see whether foaming is enhanced or reduced.

   - Is there an optimum mixture which cancels out foaming?
   - Does the mixture clean better or worse than its constituents?
   - How are mixtures of surfactants used in everyday products?
   - What other factors must be considered?
   - Why is it that when soap is put into a bubble bath, the bubbles "pop"?

2. Electrolysing various surfactants to find out where foaming takes place.



   - Would this help to classify the surfactants?
   - What about surfactants which are not charged?
   - What about mixtures of surfactants?

3. What effect does changing the pH have on either (1) or (2) above?

4. Could ion exchange be used to identify different surfactants and their properties?

5. Do different surfactants have different uses? How might the following variables be used to show this?
   (a) concentration (b) temperature (c) fabric (d) type of soiling
   (e) pH conditions (f) biodegradability (g) types of water (hard or soft)

This list is by no means exhaustive: there are many other possibilities which could be investigated.

Some Sources of Information

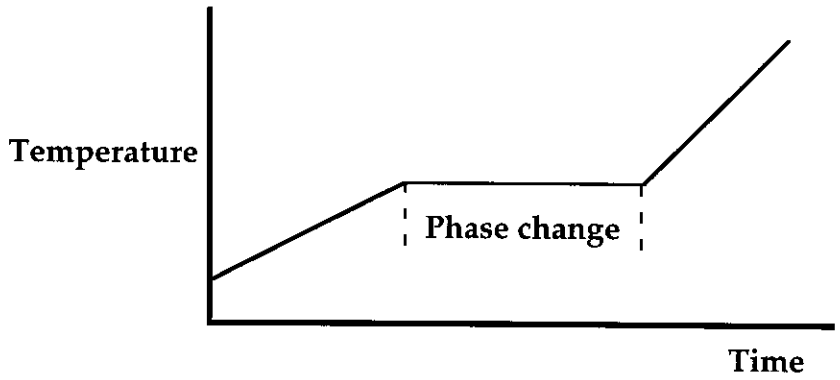
The school/college may have the "Detergents" booklet series produced by Unilever.

B.K. Selinger, *"Chemistry in the Market Place 4th Edn."*, Harcourt, Brace, Jovanovich, London, 1991

Differential Thermal Analysis (DTA)

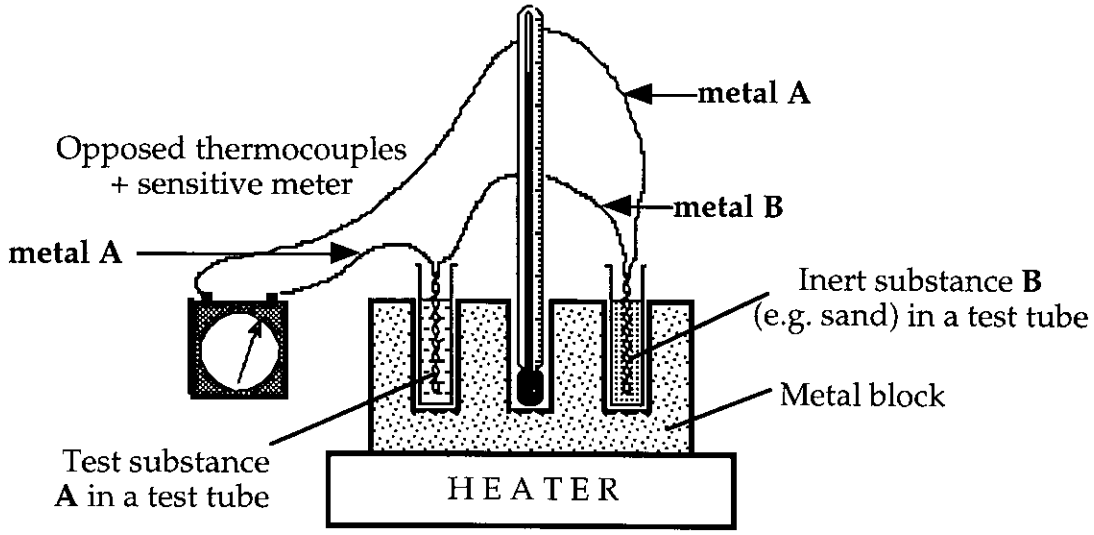
Investigation Brief

If a substance is heated at a steady rate, its temperature rises with time until a phase change such as melting or boiling occurs. While the phase change (an endothermic process) is taking place, the temperature remains constant, but when the change is complete the temperature begins to rise again.



When other endothermic processes, such as decompositions, take place, something similar happens. If these "temperature flats" can be detected, information can be obtained about the effect of heat on the substance.

One way of doing this is by Differential Thermal Analysis (DTA). If two substances - one the test substance and the other an inert substance which does not undergo changes in the given temperature range - are heated at the same rate, then any observed differences in temperature between the two substances will indicate when changes are happening in the test substance. A possible apparatus is shown below.



Since both substances are being heated in the same block, they should be at the same temperature until changes begin to take place in the test material. If the temperature differences can be detected and plotted against time, chemical information will be obtained.

Some Starter Questions

- Why are the phase changes endothermic processes?
- What actually happens at one of the phase changes?
- Why is it important to have an inert substance in the second test tube?
- What is meant by "inert" in this context?
- Does the choice of inert substance affect the experiment?
- Are both substances being heated to the same extent?
- How will any temperature differences be detected?
- What information will be obtained from the sensitive meter?
- How could the current be measured if it is very small?
- What is a "thermocouple"?
- What is an "opposed thermocouple"?
- Why are opposed thermocouples used?
- Would the type of block affect the experiment?
- Would the chosen method of heating the block affect the experiment?
- What information about the test substance is required before an effective DTA can be carried out?
- What are the thermodynamics of the changes taking place?

These are only some of the questions that could be asked. If you can think of others, please do so.

Possible Investigations

1. Design problems

   (a) The size and type of block used.
   (b) Heating by flame, on an electrical hotplate, or by building a low voltage heating coil into the block.

2. Detector problems

   (a) A pair of opposed thermocouples, with one junction in each substance, would generate a current which could be measured.
   What are the best wires to make the thermocouples - (copper/iron) or (copper/constantan) or some other combination?
   Perhaps thermistors would be better?
   (b) Since the current is very small, it needs a sensitive detector. This may allow the linking of the DTA apparatus to a computer through a suitable interface.

3. Chemical problems

   (a) Choice of inert substance.
   (b) Choice of test substances. Begin with something with a known melting/decomposition temperature e.g. $NaHCO_3$.

4. Possible substances to test include:
   (a) hydrated salts, such as $CuSO_4.5H_2O$, where the water molecules are partly behaving as ligands. DTA can be used to find out if all the water molecules come off equally easily. If so, then all are in the same environment; if not, then more than one temperature flat may be obtained. This allows information about the structure of the hydrated salt to be obtained.

   (b) plastics such as hard plastics which have a glass transition temperature (T_g) when the structure changes and the properties move from a brittle, glassy substance to a more flexible rubbery substance before it melts (T_m). However, some plastics decompose before they reach T_m and this should show in a DTA plot. T_g and T_m can be related to the uses for these plastics.

   (c) margarines/butters and spreadables could be compared and contrasted - another pupil could investigate differences between saturation and unsaturation.

   (d) some organic substances related to cholesterol have a series of "flats" in which the substance seems to melt and yet retains the properties of a crystal - in the way it reacts to polarised light, for example. These are called **liquid crystals** and form the basis of strip thermometers on which temperature numbers appear.
   Why not investigate what is going on?

This list is by no means exhaustive: there are many other possibilities which could be investigated.

Some Sources of Information

Differential Thermal Analysis

Journal of Chemical Education, 1990, **67**, 612

Thermocouples - background

A thermocouple is one of the most commonly used temperature measuring devices. It offers a low cost, simple but not very precise means of measuring temperature. Thermocouples can be used in many different environments and this makes them very versatile.

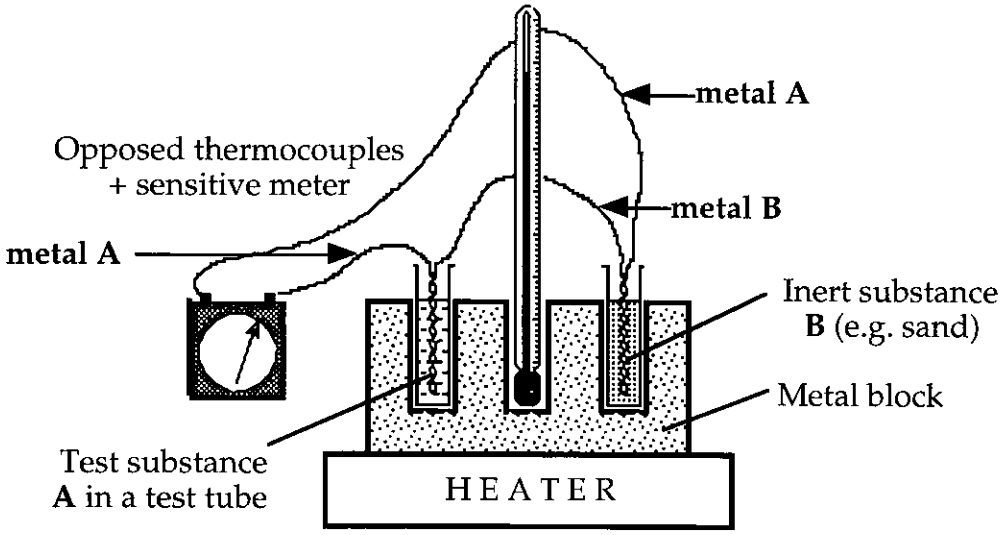
A thermocouple consists of two different metals twisted together making a continuous circuit. This produces an electromotive force (emf) or voltage between the two metals. In practice two junctions are normally used. If one junction has a different temperature from the other, an emf is established. This voltage varies with the difference in temperature between the junctions. If the temperature at one junction is known, the temperature at the other junction can be found.

A simple thermocouple for this experiment can be established using copper and copper/nickel (Constantan). The junctions are produced by twisting the two dissimilar metals together. One thermocouple is placed in the sample the other in the inert substance in the other hole in the metal block.

As the test sample starts to heat up it will be at the same temperature as the inert substance. With the thermocouple junctions being opposed the two emf's oppose one another, so there is no current. However, when the sample begins to decompose there will be a difference in temperature between the sample and the inert substance and so a small electromotive force is created, leading to a reading on the meter.

Help and Hints

The home made apparatus consists of a block of metal (aluminium works well), with dimensions roughly 10cm by 8cm by 7cm, with three holes drilled symmetrically into it. The centre one should be just large enough to take a thermometer; the other two the small test tubes. The thermometer used should be of the required range for the test substance; it could be an ordinary bulb thermometer or an electronic thermometer. It is also a good idea to add a small quantity of powdered copper metal to the three holes to improve the contact between the metal block, the two test tubes and the thermometer.



The meter used could be a galvanometer, electronic meter such as avometer EA113 or the apparatus may be linked to a data-logging device.

One possible investigation would be to use the hydrated salt copper sulphate ($CuSO_4.5H_2O$). Do all the water molecules come off at once (one "flat") or in stages? Examination of the structure of this salt will help to explain the results obtained.

It is possible to predict the temperature of decomposition using thermodynamics. The decomposition is feasible when the Gibbs free energy of formation (ΔG°_f) is zero or negative. The decomposition temperature can be calculated using the equation:

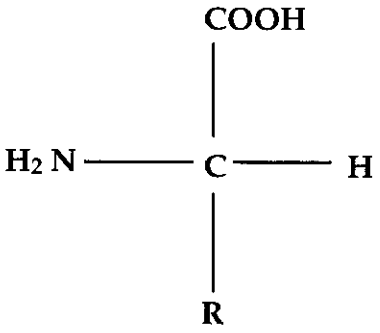
$$\Delta G^\circ_f = \Delta H^\circ_f - T\Delta S^\circ$$

Electrophoresis

Investigation Brief

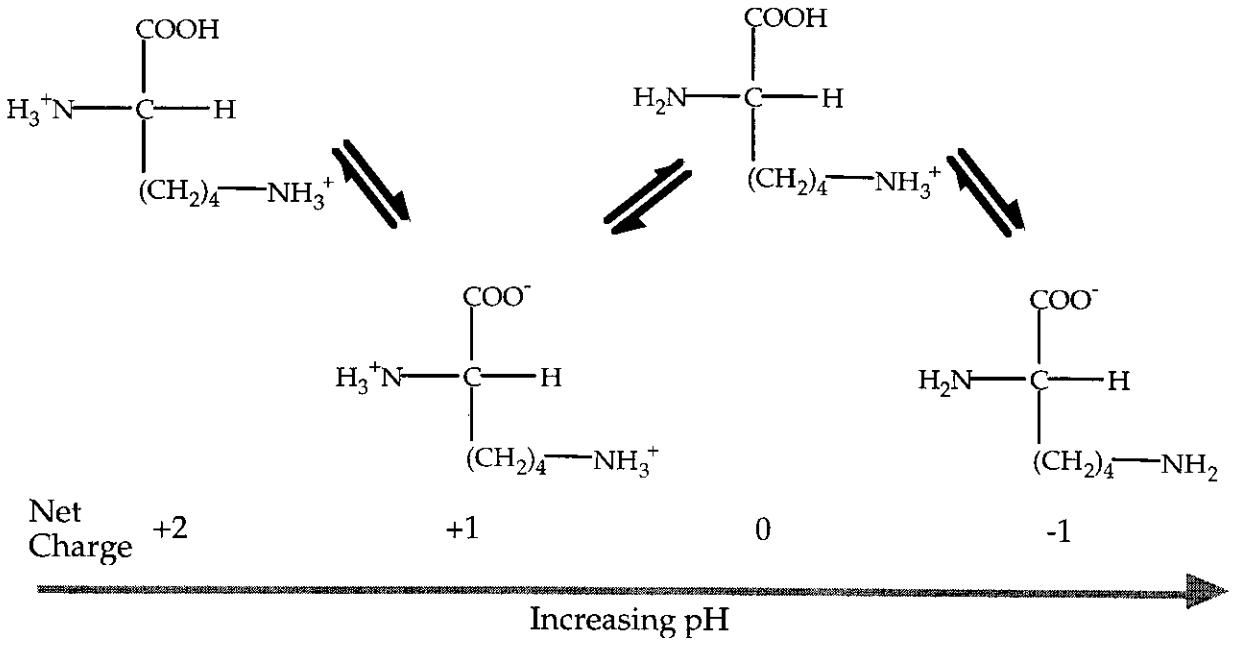
Proteins are composed of amino acids joined together by covalent (peptide) bonds to form polypeptides.

An amino acid has the structure:



There are a large number of amino acids, but about 26 are found in human protein. Each amino acid has a unique side chain (R), which gives a characteristic shape, size, polarity and charge.

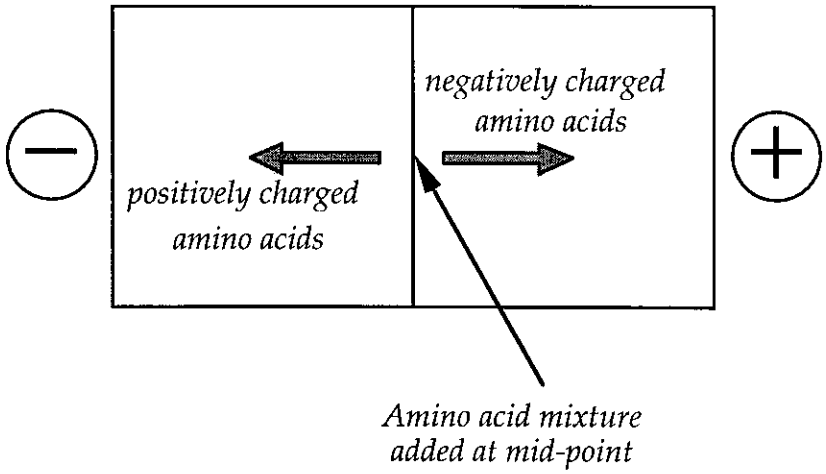
The presence of an acidic group COOH and a basic group NH_2 in each amino acid means that the amino acid has a charge which is dependent upon the pH. In acidic solution the basic group reacts giving a positive species (similar to ammonium NH_4^+); conversely in alkaline solution, the acidic group reacts giving a negative species CO_2^-. Consider, for example, the effect of pH on lysine (where R=$(CH_2)_4NH_2$) shown below:



The overall charge on an amino acid in a solution is determined by the pH and type of functional group on the side chain, R.

If the side chain R contains a carboxylate group, the overall charge on the amino acid would be different to lysine at most pHs. The pH at which an amino acid is neutral overall is called the **isoelectric point**.

For a particular mixture of amino acids, a pH can usually be found such that some amino acids are positively charged, some negatively charged and some neutral. If this mixture is added carefully to a strip of filter paper (soaked in buffer at the appropriate pH), and this paper is suspended between two electrodes, the following would happen:



The pH buffer also acts as an electrolyte to enable efficient migration of the amino acids in the electric field. The polarity and size of the R side chain also affects the interaction with the cellulose in the paper and hence the migration rate through the paper.

This process is called **electrophoresis**. When the stationary phase used is a paper similar to filter paper, it is called paper electrophoresis.

Using a power supply, an electrical potential is applied to opposite ends of the paper soaked in the buffer. Amino acids with a net positive charge migrate to the cathode and those with a net negative charge move towards the anode. Due to the interactions of the **R** groups with the paper not all amino acids of the same charge travel at the same rate towards the electrode. These allow separation of the amino acids on the paper.

The buffer has two main functions:

(i) to buffer against pH change, which occurs during the electrophoresis because acid is produced at the anode and base at the cathode.
(ii) to form a conducting ionic connection between the electrical supply (electrodes) and the suspension medium (paper).

Following electrophoresis, the amino acids may be made visible by a number of different staining methods using chemical reagents such as ninhydrin.

Some Starter Questions

- What is a "peptide bond"?
- What is a "polypeptide"?
- What amino acids are found in human protein?
- Is the charge of a particular amino acid only dependent on pH?
- Does the side chain have an effect on the overall charge at a given pH?
- Does the overall size and shape of the molecule affect the charge at a given pH?
- Does the overall size and shape of the molecule affect the pH?
- Does the overall size and shape of the molecule affect the rate of migration to the electrodes?
- What about the neutral amino acids?
- What is the purpose of the electrolyte?
- How does the pH buffer act as an electrolyte?
- How does the buffer act to prevent changes in pH?
- Why is a developer such as ninhydrin used to locate the amino acids?
- What is meant by the "stationary phase"?
- How can amino acids be produced from proteins?

These are only some of the questions that could be asked. If you can think of others, please do so.

Possible Investigations

1. Electrophoresis can be used to help identify amino acids present in the proteins in various foodstuffs.

   - How could the amino acids be obtained from the foodstuffs?
   - How could they be identified?
   - Are there amino acid standards which could be used as references?

2. Factors affecting the separation of amino acids.

   - Is the voltage applied to the electrophoresis cell important?
   - Is there an optimum voltage?
   - How does the pH affect the separation?
   - Is the temperature important?
   - Does the type of paper used affect the separation of amino acids?

3. Determine the amino acids present in natural fibres, for example wool or hair, by electrophoresis.

   - Does the type of fibre make a difference to the amino acids present?
   - Does dyeing the fibre have any effect on the amino acids?
   - Are the amino acids affected by bleaching?

4. Similar separations of transition metal ions can be achieved using Na_2SO_4 solution instead of the buffer. Coloured ions may be easily visible but exposure to ammonia gas may help. Colourless ions can also be located by spraying the paper with another ion which reacts to give a coloured compound. For example, Pb^{2+} sprayed with KI gives yellow PbI_2.

   - Could traces of metal ions be detected by electrophoresis?
   - Can mixtures of transition metal ions be separated by electrophoresis?
   - How would this compare with ion exchange?

This list is by no means exhaustive: there are many other possibilities which could be investigated.

Some Sources of Information

B.K. Selinger, "*Chemistry in the Market Place 4th Edn.*", Harcourt, Brace, Jovanovich, London, 1991

Instruction manual for the commercial electrophoresis apparatus being used.

Instruction manual for any data-logging apparatus being used.

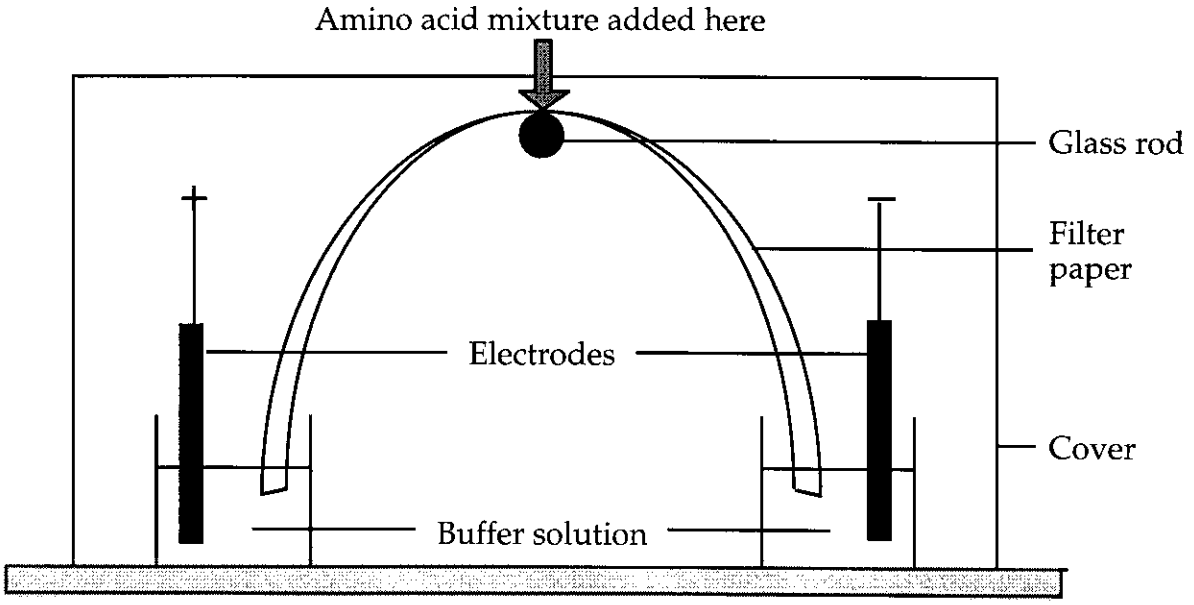
Help and Hints

PAPER ELECTROPHORESIS

It is important to be aware that there are various commercial electrophoresis set-ups which may differ in detail from the description given.

A strip of filter paper is soaked in a buffer solution and suspended, at its mid-point, over a glass rod with its ends dipping into two beakers of the same buffer.

The mixture is applied to the mid-point of the filter paper, and a potential difference (p.d) of about 30V is applied across the electrodes. The whole apparatus is enclosed under a cover such as a large glass beaker or trough **and left for several hours to allow the atmosphere to become saturated with the solvent and hence prevent evaporation of the solvent from the filter paper before running the experiment**. The amino acids will migrate towards the electrode of the opposite charge, or stay at the mid-point if they are at their isoelectric point at the pH of the buffer. By using buffers of different pH, different amino acids will move or remain stationary, and different separations will take place.



After about an hour, the paper can be dried with a hair dryer and then sprayed with ninhydrin and heated to reveal the positions of the amino acids.

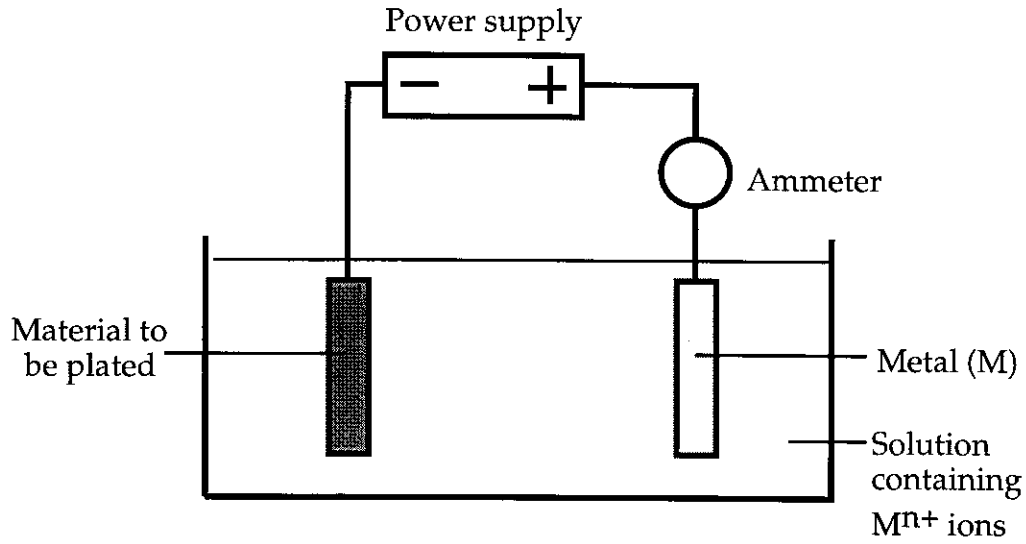
CAUTION : ***Ninhydrin should be handled with care.***
Avoid contact with the skin.
Wear gloves while handling it and use it in a fume hood.

Electroplating

Investigation Brief

Electroplating is widely used in industry to deposit one layer of metal on top of another metal, alloy, plastic or even plant material. Engineering components which have been over-machined, or which need a tough wear-resistant surface, can be electroplated. Thin layers of gold, silver or chromium can be used to plate articles made from less expensive metals to improve their appearance and/or durability and as a means of preventing corrosion. Fine cutlery, for example, is silver-plated electrochemically.

A simple electroplating bath would look like the diagram below.



If metal electrodes are used in the electrolysis of an aqueous solution, the electrode will oxidise if its oxidation potential is more positive than that of water. For example:

Anode $\quad Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^- \qquad E^\circ = +0{\cdot}25V$

$\qquad 2H_2O(l) \longrightarrow 4H^+(aq) + O_2(g) + 4e^- \qquad E^\circ = -1{\cdot}23V$

So a nickel anode will be oxidised. The metal will be dissolved from the anode, be reduced at the cathode and deposited there, creating the protective layer.

Cathode $\quad Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$

Composition is the most important aspect of electroplating and a number of solutions may have to be tried to get the bath composition that works effectively.
Baths of copper, zinc and nickel can be used. Common baths of these metals have names such as Bright Acid Copper Bath, Neutral Chloride Zinc Bath and Watts Bath.

Some Starter Questions

- How accurate are predictions based on E° values, as above?
- How will the type of solution affect the electroplating of a metal?
- How will the pH of the solution affect the electroplating of a metal?
- How will the relative positions of the metals in the electrochemical series affect the electroplating of a metal?
- How will the voltage used affect the electroplating of a metal?
- How will the type of electrodes affect the electroplating of a metal?
- How will the length of time that the current is passed affect the electroplating of a metal?
- Which metals are the best for plating?
  What is meant by "best"?
- Which metals are the easiest to plate?
  What is meant by "easiest"?
- What other factors should be considered to obtain a firm adherent coating of metal?
- What else could be produced at the cathode and anode during electroplating?
- What is a "Bright Acid Copper Bath", a "Neutral Chloride Zinc Bath" and a "Watts Bath"?

These are only some of the questions that could be asked. If you can think of others, please do so.

Possible Investigations

For any investigation, the correct composition of the bath is essential for successful electroplating.

1. Successful electrodeposition only occurs within specific ranges of current density (current per unit area of the cathode) and bath temperature.

   - How could it be decided if deposition had been "successful"?
   - Can a test be designed for this?
   - What are the limits of successful deposition?
   - Which of the two factors (current density and temperature) is more important?
   - Are the limits constant for the material being plated, regardless of the metal being deposited, or vice versa?

2. Choose one metal to be the base metal and vary the metal deposited.

   - What combinations should give the best corrosion protection?
   - How could you evaluate this to find if theory and practice agree?
   - Does a second metal plating of either the same or a different metal, deposited on the first metal plating, make any difference?

3. Frequently the deposited layer is dull and matt in appearance.

   - Can the metal be polished physically?
   - Can the metal be polished in situ in the bath?

4. Can the thickness of the metal deposited be measured?

   How efficient (in terms of current used and metal deposited) is your experimental set up?

5. Small plastic components, such as bathroom fittings, are often electroplated to enhance their appearance, or, in the case of electronic components, to provide screening from external radio signals.

   A copolymer, such as ABS (acrylonitrile-butadiene-styrene) can be plated. If this plastic is immersed in hot, concentrated sulphuric acid for around 15 minutes, its surface will be etched. This means microscopic pockets are formed on the surface into which metal coatings can be attached.

   The plastic is given a conducting coat with a solution of carbon particles, such as Aquadag, and allowed to dry. Electroplating can then be carried out as above.

   Together with the usual variables for deposition, the etching can also be examined.

   - Is there an optimum time for etching?

- Are other acids as effective as sulphuric acid?
- Can the etching on the surface be seen through a microscope?

6. Plant material, such as ivy leaves, can be electroplated to produce jewellery.

   A leaf, sprayed with lacquer to stiffen it, coated with a conducting paste, can be electroplated in the usual way.

   All the above factors could be examined, although the appearance of the plated layer (see 3 above) would be of particular importance in jewellery production.

This list is by no means exhaustive: there are many other possibilities which could be investigated.

Some Sources of Information

Kirk-Othmer, *Encyclopedia Of Chemical Technology*, 3rd Edn, John Wylie and Sons, 1983, **8**, 826

"Electroplating: Economic Awareness and Enterprise" by M.Thomas, *School Science Review*, 1991, **72**, 147

Help and Hints

The following recipes are good starters for the practical work.

(1) *For copper* — *Bright Acid Copper Bath*

100g of copper(II) sulphate,
50 cm^3 of 2 mol l^{-1} sulphuric acid, and
3g of copper(II) chloride in 500 cm^3 of water.
Bath at room temperature.
Anode of copper.

(2) *For zinc* — *Neutral Chloride Zinc Bath*

120g of zinc sulphate,
7.5g of ammonium chloride, and
15g of aluminium sulphate in 500 cm^3 of water.
Bath at room temperature.
Anode of zinc.

(3) *For nickel* — *Watts Bath*

52.5g of nickel(II) sulphate,
7.5g of ammonium chloride, and
7.5g of boric acid in 500 cm^3 of water.
Bath at 35°C.
Anode of nickel.

To obtain a firm coating, the base metal must be completely clean. Tarnished or corroded surfaces should be cleaned with emery paper. Final preparation can be done by immersing in dilute nitric acid for a few moments and/or degreasing with propan-2-ol. Note that these are temperatures at which the baths will work, not necessarily the best temperatures.

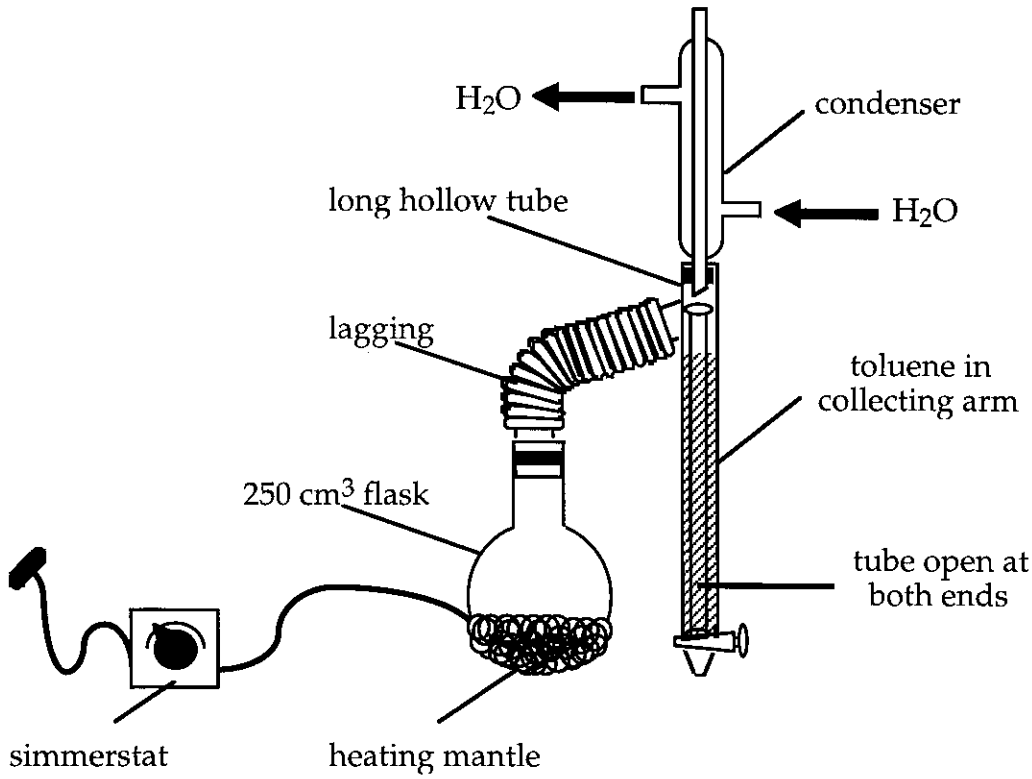
Fat and Water in Food

Investigation Brief

In the last few decades there has been increasing concern over the fat content of foodstuffs, particularly of saturated fat in dairy products and meat. It is hardly possible these days to buy margarine, butter or cheese without being confronted with information on its mono, di and poly unsaturated fat content. Indeed, manufacturers have even taken to proclaiming 'low fat' on such products as breakfast cereals, despite the fact that these foods have always contained very little fat.

The Dean and Starke apparatus allows for quantitative determination of the water and fat content of foodstuffs. In the apparatus, the foodstuff concerned is mixed with methylbenzene (toluene) and water, and distilled. The two solutions do not mix - boiling occurs at 100°C, with both water and toluene in the vapour

Distillation carries over the toluene, the water and fat from the food in the form of an azeotrope (constant boiling mixture). After condensing, two layers - an aqueous bottom layer (with 0.06% toluene dissolved) and an organic top layer (with 0.05% water dissolved) are formed. The fat from the foodstuff is dissolved in the toluene and can be isolated and weighed.

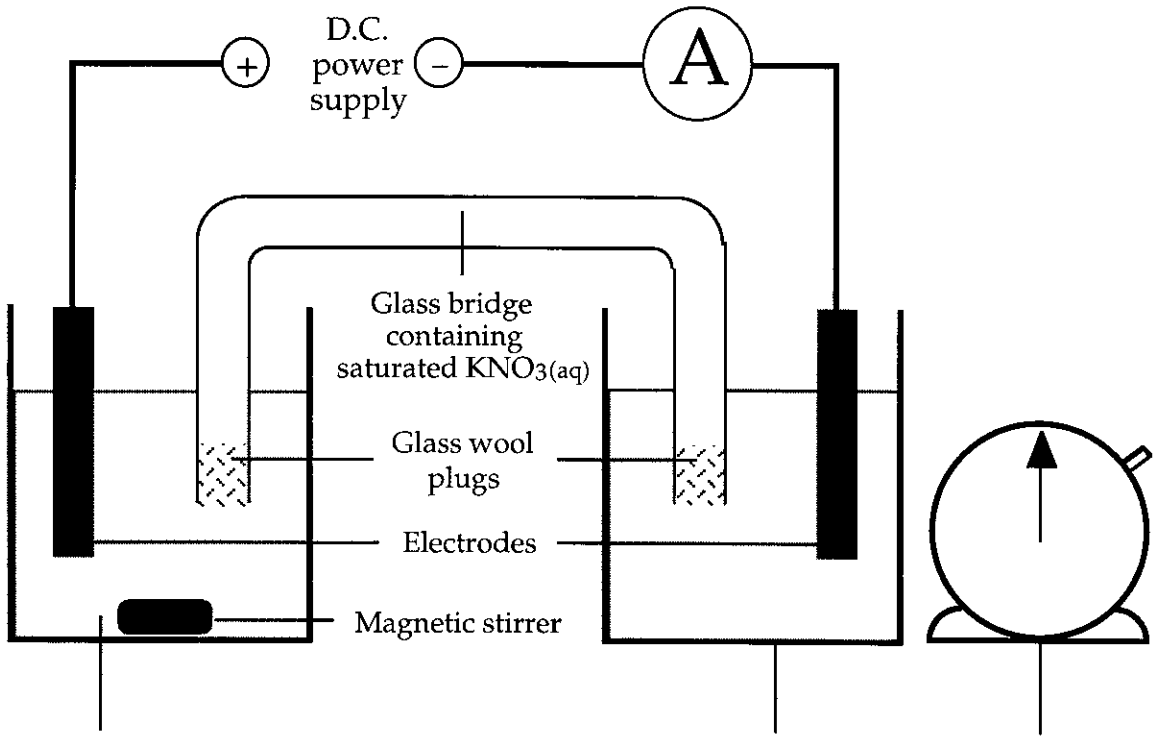


Dean and Starke Apparatus

A Dean and Starke apparatus only allows for the separation of the fat from the foodstuff. In order to investigate the degree of saturation, so called "iodine numbers" are determined. An iodine number is defined as

the number of grams of halogen, calculated as iodine, which binds to 100g of fat.

The standard method of determining iodine numbers involves toxic chemicals unsuitable for use in schools. However, a cleaner and safer method is available, involving coulometric titrations (titration with electrons). In practice electrolytically generated bromine is added across the fat's double bonds. Bromine is used in preference to iodine because of steric problems (see standard textbooks for an explanation.)



As it is produced, the bromine generated at the anode reacts with the unsaturated fat or oil. Consequently the cell solution remains colourless until the fat is saturated with bromine. Immediately after the point of saturation, a faint brown colour is observed.

When the saturation point has been reached, the current and the stopclock are switched off. The current and time to reach saturation is recorded. Some solid KI is added: the excess bromine displaces an equivalent amount of iodine:

$$Br_2(l) + 2I^-(aq) \longrightarrow 2Br^-(aq) + I_2(aq)$$

The iodine released is titrated with standard thiosulphate solution using starch solution as an indicator to detect the end-point.

$$I_2(aq) + 2[S_2O_3]^{2-}(aq) \longrightarrow [S_4O_6]^{2-}(aq) + 2I^-(aq)$$

Some Starter Questions

- What is the difference between "saturated" and "unsaturated" fats?
- What is the difference between mono, di and poly unsaturated?
- What does the word "qualitative" mean?
- An azeotrope is a constant boiling mixture. What does this actually mean?
- Why does the fat become dissolved in the toluene?
- Why does the fat not dissolve in the water?
- How does a coulometric titration work?
- What does the text mean by "steric problems" and why are they more pronounced with iodine than bromine?
- Why should it be easier to add bromine compared to iodine across the double bond?
- Why does bromine displace iodide ions from potassium iodide to release iodine?
- Why is starch a useful indicator in the titration of iodine produced with the thiosulphate solution?
- Is the magnitude of the current an important factor in the experiment?
- What information about the standard thiosulphate solution do you need to know to be able to calculate how much iodine has been produced?

These are only some of the questions that could be asked. If you can think of others, please do so.

Possible Investigations

1. Comparison of the fat and water content of low and high fat foodstuffs e.g high/low fat crisps, high/low fat ice cream.

   - Just how low *is* low fat?
   - What replaces the fat in low fat foods? Is this different in different foods?

2. Many foodstuffs are bulked up with additional water - bacon is a good example - it is injected with phosphate solution. The label tells us how much is injected, but does not include the water absorbed during the curing process. This is an expensive way to buy water! It is particularly easy to increase the net weight of frozen foodstuffs by adding water.

   - How much water is there in frozen foods?
   - How much fat does the frozen food contain?
   - How does the fat and water content of the frozen food compare with a fresh sample of the same foodstuff?
   - How is the "25% extra free" advertised on many frozen products composed? Are we getting more produce or more water?

3. Often people pay extra money for meat which they think contains less fat. Is there much difference between the fat content of burgers and sirloin steak?

   - Is there a difference between normal and lean meat?

   - Is there a difference between meat products advertised as low fat and normal meat products?

   - Does buying meat from a butcher or from a supermarket affect the fat content?

4. More and more people are eating white meat, like chicken, in preference to red meat, like beef, believing that it contains less fat or more healthy fat. Is this belief true?

This list is by no means exhaustive: there are many other possibilities which could be investigated.

Some Sources of Information

A Method of calculating the degree of unsaturation - using Iodine numbers

If a current of **I** amp has been applied for **t** seconds, the number of moles of bromine generated is given by the formula $\frac{I\,t}{2\,F}$

where **F** is the Faraday constant = 96,500C mol^{-1}.

This amount of bromine has done two things:

(i) some of it has gone to saturate the fat,
(ii) some of it is the excess which reacted with KI to give I_2. Call this **y** moles.

The number of moles of bromine used by the fat must be $\left(\frac{I\,t}{2\,F} - y\right)$

A value for **y** can be found from the thiosulphate titration because 2 moles of thiosulphate are equivalent to 1 mole of I_2, which is equivalent to 1 mole of Br_2.

Now knowing **y**, $\left(\frac{I\,t}{2\,F} - y\right)$, the number of moles of bromine taken up by the fat can be calculated.

If the mass and molecular mass of the fat are known, the number of moles of bromine taken up by one mole of fat and hence the number of double bonds can be calculated.

This data is used to calculate the iodine number, i.e. *the number of grams of halogen, calculated as iodine, which is absorbed by 100g of fat.*

Before using this procedure to investigate the degree of saturation of an extracted fat, the overall efficiency of the cell should be checked with a fatty acid of known saturation, such as oleic acid. If necessary, a correction factor can then be introduced to the measurement of the unknown fats.

For the Basic Dean and Starke Apparatus (without modifications made in this text)

B.K. Selinger, "*Chemistry in the Market Place 4th Edn.*" (or later editions), Harcourt, Brace, Jovanovich, London, 1991

For Phase Diagram about azeotropic mixture

"Water, Water, Everywhere" by B.K. Selinger, *Education in Chemistry*, 1979, **16**, 125

For Iodine Numbers Background

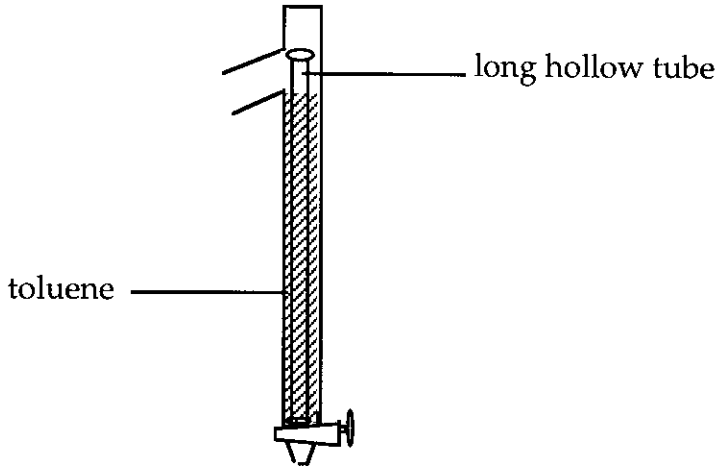
H. D. Belitz and W. Grosh, "*Food Chemistry*", Springer-Verlog, London, 1987

Help and Hints

Determination of water and fat content of various foodstuffs using the Dean and Starke Apparatus

1. Approximately 20g of foodstuff is distilled with 80 cm^3 of toluene in the flask.

   The collecting arm is filled at the start with toluene and a long hollow glass tube is placed into the collecting arm, the length of the tube is such that the top lip lies just below the reflux condenser but clear of the toluene in the collecting arm. This is done to prevent the water and toluene mixture spilling back over into flask. When the water-toluene mixture condenses, it runs through the tube and accumulate at the bottom of the collecting arm. This allows the separation of the two component layers - the aqueous layer is the lower layer and thus only the less dense toluene can run back into the flask.



2. When the distillation is complete, after 20 minutes or when no more water can be seen to be distilling over, the water in the collecting arm is run off, giving the water content of the foodstuff. If the liquid in the collecting arm is milky, making it difficult to see the line between the two layers, add a little salt. This should make for quicker separation. Why? (Hint - think of soap)

3. To determine the fat content of the foodstuff, the toluene solution in both the flask and collecting arm is carefully poured into a weighed beaker. Several additions of toluene are made to the foodstuff left in the flask, and shaken to remove any remaining fat, and each toluene/fat solution added to the solution already in the pre-weighed beaker.

4. Finally, the toluene is evaporated in a fumehood over a water bath and under a water pump vacuum until only the fat remains. The beaker is then reweighed to determine the fat content.

CAUTION : ***Toluene vapour is slightly toxic and so, if there is no fume hood available, you should use cyclohexene instead. It should be noted, however, that cyclohexene is not such a good carrier of water. Both solvents are flammable and present a fire hazard.***

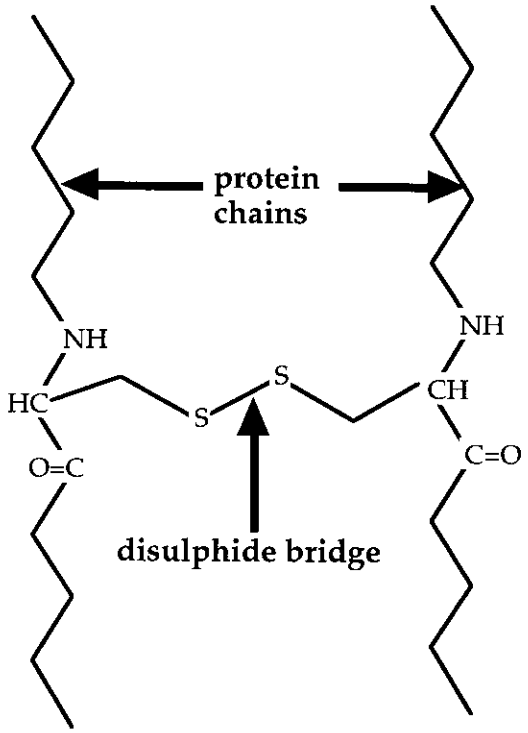
Hair

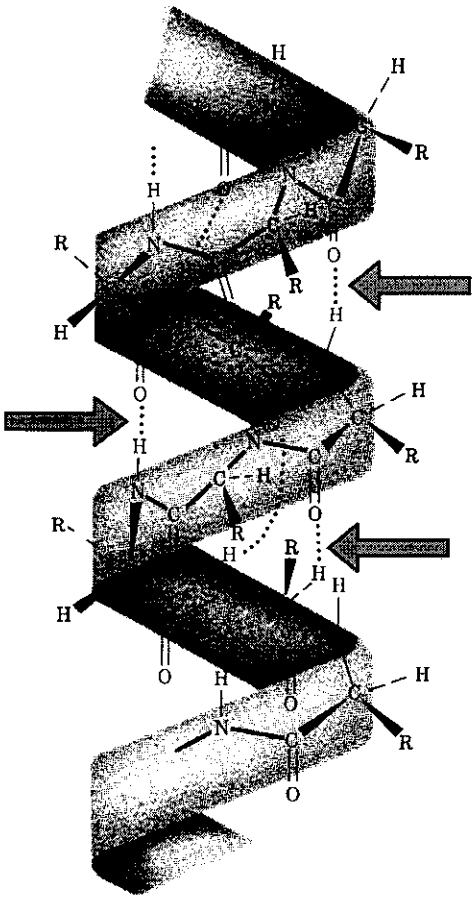
Investigation Brief

Hair is composed of the structural protein α-**keratin**. This protein exists in an α-helical form and is rich in cystine, the oxidised form of the amino acid cysteine.

The cystine, which exists as a dimer, forms disulphide bridges with the residues in other α-helices which then coil around each other to form multiple strands.

The disulphide bridges act by stabilising the protein structure. When a cystine residue in one α-helix combines with a cystine residue in the **same** keratin strand, the hair becomes curly.





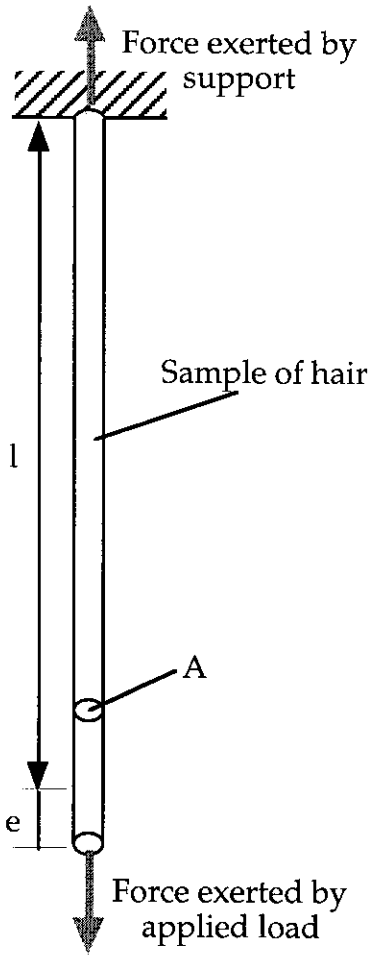
The general appearance of the α-helix structure is similar to a coiled telephone cord. Successive turns of the structure are linked together by hydrogen bonding between the amino group on one turn and the carboxyl group on the next turn. It is this hydrogen bonding which enables hair to stretch.

If a tensile (stretching) force is applied to the hair fibre, the relatively weak hydrogen bonding breaks and the α-helix stretches out as it untwists.

When force is removed, the helix coils up again and the hydrogen bonding is re-established between the successive turns of the coiled hair fibre. This gives hair its natural elasticity.

Tensile Strength of Hair

The tensile strength is a measure of how great a stretching force the hair can withstand without breaking. To enable fair comparisons to be made between hair samples of different lengths and thicknesses, the terms (tensile) stress and (tensile) strain are used when referring to the deforming force and the deformation produced.



Stress is the force acting on unit cross-section area.

Thus, the tensile stress = F/A.

The unit of stress is the Pascal (Pa) or Nm^{-2}.

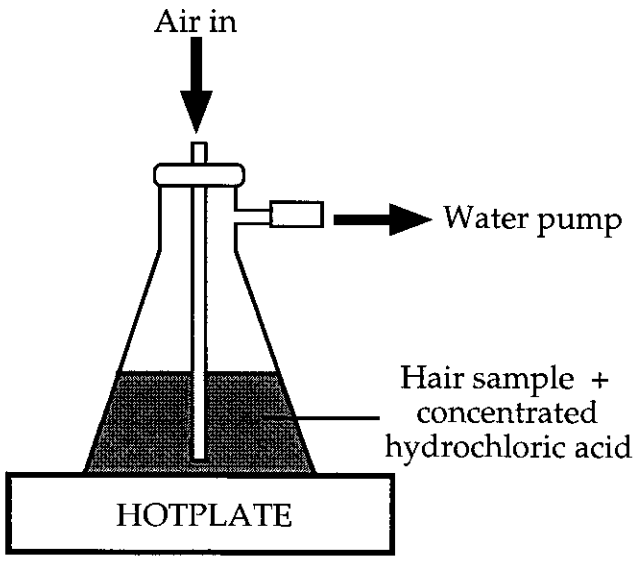
Strain is the extension per unit length.

Thus, the tensile strain = e/l

Strain is a ratio and has no units.

where **F** = applied force (N)
A = cross section area (m^2)
e = elongation (m)
l = length of sample being stretched (m)

The Hydrolysis of Hair



A simple hydrolysis can be used as a means of obtaining the different amino acids from a sample of hair. Hydrolysis can also be used as a technique when examining the chemical treatment of hair during washing, dyeing, perming etc. Hydrolysis of different types may yield different products.

The amino acids can then be examined using techniques such as paper electrophoresis to separate them according to the size and type of charge they carry, or by using chromatography.

Some Starter Questions

- What is a "protein"?
- What is "keratin"?
- What is an "amino acid"?
- What is "cysteine"?
- What is a "dimer"?
- What is a "disulphide bridge"?
- What is the "hydrogen bonding"? Why is the hydrogen bonding important?
- How does hydrogen bonding allow stretching?
- What is meant by "tensile strength"?
- How might the tensile strength be measured?
- What is a "determining force"?
- How is hydrolysis carried out?
- Why is hydrolysis necessary?
- Why is hair coloured?
- What is "paper electrophesis" and how might it be used to separate amino acids?
- What is "chromatography" and how might it be used to separate amino acids?

These are only some of the questions that could be asked. If you can think of others, please do so.

Possible Investigations

1. Comparison of the tensile strengths of human hairs of different colour, racial origin, age, gender, degree of curliness or from different parts of the body.

2. Comparison of the tensile strength of human hair with that of other natural fibres, such as dog hairs, horse hairs, silk threads, spiders' webs etc.

3. Does frequent washing affect the strength of hair?

4. Does frequent cutting affect the strength of hair?

   Shaving /cutting hair might affect how it grows. Compare hair from a head, from a beard, from under the arm or from the chest, all from the same person.

5. Do shampoos and conditioners affect the strength of hair?

6. How does chlorinated water in a swimming pool affect the keratin fibres in hair?

   If you have a school swimming pool you could use it to see what effect the chlorinated water has on a number of test subjects within your school.

7. What effects do changes in pH have on the properties of hair? Are the amino acids present in hair affected by the change?

This list is by no means exhaustive: there are many other possibilities which could be investigated.

Some Sources of Information

Generating the conditions of a swimming pool in the laboratory.

It is possible to simulate the conditions of a swimming pool by placing the hair sample in a beaker containing a chlorinating solution like that in a swimming pool. For example, 0.01g of hair soaked in 2 cm^3 of a 10ppm solution of sodium hypochlorite in water for approximately 1 hour. The sample is then removed and left to dry in the air for a further hour.

"Synthetic" swimming pool water consists of a 10ppm solution of sodium hypochlorite.

N.B. 10ppm (parts per million) means:
10g solid in $1x10^6$ g of solution (or water)
or 0.1g solid in $1x10^4$ g or 10^4 cm^3 or 10 litres of water

Help and Hints

Tensile Strength

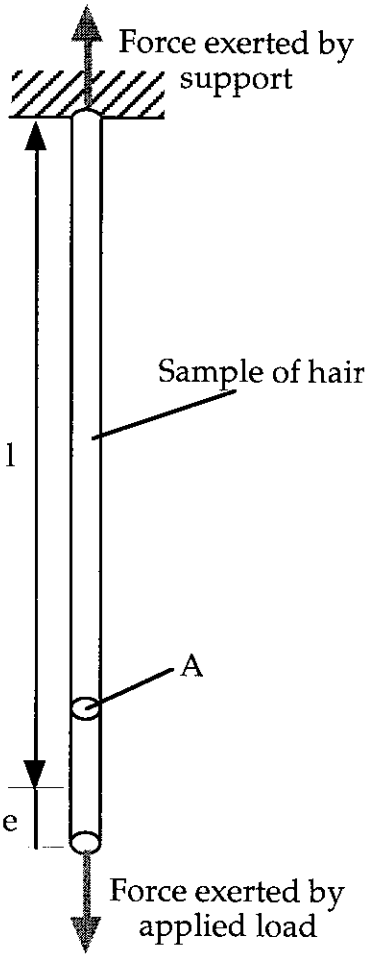
Using a micrometer screw gauge, the diameter of the hair sample is measured at several different places along its length. The average diameter and hence the mean cross-section area is calculated.

The hair sample is fixed securely to a clamp stand using bulldog clips so that it does not slip when the stretching force is applied. This is essential since the exact amount that the sample stretches is being measured, and any 'slippage' at the support could introduce serious error in this measurement.

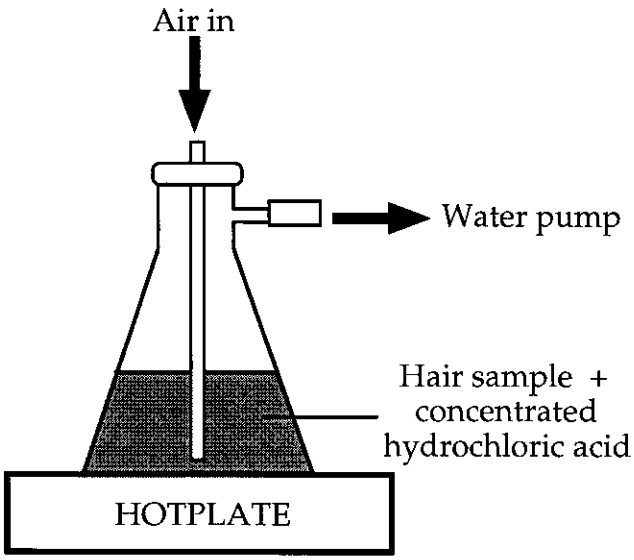
A 100 cm^3 plastic container is securely attached to the lower end of the hair sample. This by itself should remove any 'kinks' from the sample, but it may be necessary to add some water to the container to fully straighten the sample. The starting length of the sample is then measured using a millimetre scale.

Measured volumes of water are added to the plastic container at regular intervals and the length of the hair sample measured each time. This procedure is repeated until the hair breaks.

Using the data collected, the corresponding stress and strain values can be calculated and a graph of stress against strain can be drawn.



Hydrolysis of Hair



Carry out these steps in the fume hood

1. A good sized tuft of hair is boiled for 20 minutes in concentrated hydrochloric acid. This breaks down the protein into constituent amino acids.

2. The solution is then heated with a stream of air bubbling through until it has reduced to a syrupy mixture.

3. Water is then added and the process repeated to remove any remaining acid. (Acid interferes with the subsequent separation process.)

Ion Exchange

Investigation Brief

Ion exchangers, as the name suggests, are systems which allow ions of a given charge to exchange with ions of the same charge in such a way as to preserve electrical neutrality.

In nature, many naturally occurring rocks (such as zeolites) exchange positive ions and affect the ions which are free in the biosphere.

In the laboratory, ion exchangers are usually found as small plastic beads (resins) which are water insoluble, cross linked, solid electrolytes. They have a three-dimensional polymer network with functional groups attached which can take part in the exchange process.

Consider a strong acid cation exchanger - ● = resin bead

$$\bullet\text{-}SO_3^- H^+(s) + Na^+(aq) \rightleftharpoons \bullet\text{-}SO_3^- Na^+(s) + H^+(aq)$$

This is an equilibrium that can be driven to one side or the other depending on the relative amounts of ion present.

This could exchange with other ions -

$$2(\bullet\text{-}SO_3^- Na^+)(s) + Cu^{2+}(aq) \longrightarrow (\bullet\text{-}SO_3^-)_2 Cu^{2+}(s) + 2Na^+(aq)$$

The resin can then be returned to its original acid form -

$$(\bullet\text{-}SO_3^-)_2 Cu^{2+}(s) + 2H^+(aq) \longrightarrow 2(\bullet\text{-}SO_3^- H^+)(s) + Cu^{2+}(aq)$$

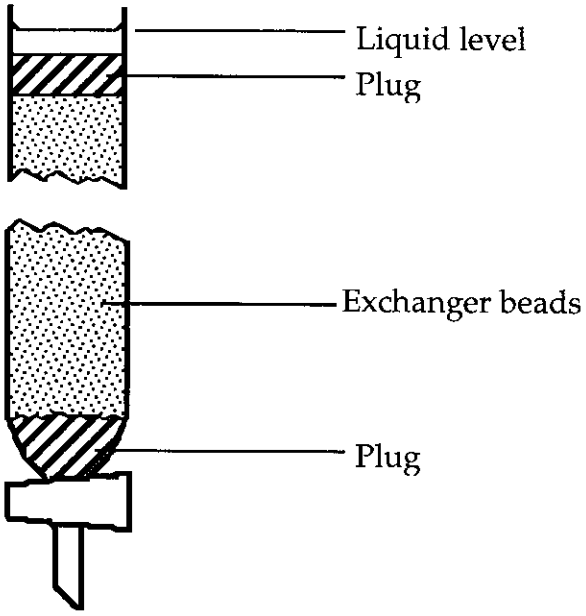
This exchange cycle can be repeated many times.

There are also weak acid cation exchangers in which the functional group is -COOH instead of -SO_3H. Similar anion exchangers exist based on ammonium.

These exchanges are quantitative and so one mole of $Na^+(aq)$ ions will exchange for one mole of $H^+(aq)$ or 0.5 moles of $Cu^{2+}(aq)$ to preserve electrical neutrality.

This gives a quantitative method for measuring ions in a solution. If the solution reacts with an exchanger in the hydrogen form, an equivalent number of moles of $H^+(aq)$ will be released which can be measured by titration with a base.

The most convenient way to handle the exchanger is in a column, such as a burette. The liquid at the top should be kept at a reasonable level above the plug to prevent the exchanger beads from drying out.



Some Starter Questions

- What is a "zeolite"?
- What is the "biosphere"?
- What other rocks exchange ions?
- What is an "electrolyte"?
- What is meant by the term "cross linked"?
- What functional groups are present in a resin?
- Are commercial resins the same as natural ones?
- What is meant by "quantitative"?
- How can titration be used to measure the number of moles of $H^+_{(aq)}$ released?
- How would you detect the end-point of this titration?
- How is the sodium ion removed from the column?
- How are ion exchangers used commercially?

These are only some of the questions that could be asked. If you can think of others, please do so.

Possible Investigations

1. Analysis of water from effluents, rivers, foodstuffs, sea shells, sea water etc.

2. Distillation is an expensive method of making "pure" water because it requires a lot of energy. Ion exchange beads can be used in its place. Suggest how this might be done and how it works by designing an exchanger to produce fresh water from salt water for use in a life raft.

3. Separation of complexes of transition metals.

   If about 5 mg of each of the following [Mn^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Zn^{2+}, Ni^{2+}] are dissolved in 1-2 cm^3 of concentrated HCl (11-12 mol l^{-1}), most of the metal ions form complexes with chloride ion to give an anion, for example $[MCl_6]^{4-}$.

   However, Ni^{2+} does not, and if the mixture is passed into an anion exchanger, Ni^{2+} is not absorbed and comes through the column washed with conc. HCl, while all the others are held. If the concentration of the HCl is now reduced, the complexes become cations and are washed out of the column in order.

   $$[MCl_6]^{4-}(aq) + H_2O(l) \longrightarrow [M(H_2O)_6]^{4-}(aq) + Cl^-(aq)$$

6 mol l^{-1}	HCl	removes	one of the ions
4 mol l^{-1}	HCl	removes	another
2.5 mol l^{-1}	HCl	removes	another
0.5 mol l^{-1}	HCl	removes	another
0.005 mol l^{-1}	HCl	removes	another

   Not all of the ions give a complex of the form $[MCl_6]^{4-}$. A literature search is suggested in order to find out the actual formulae of the complexes.

4. Can ion exchange resins be used to make fuel cells?

5. Amino acids can be anions or cations depending upon pH, and so it should be possible to separate them on ion exchange columns at different pH values. A process similar to that used in (3) above could be used with buffers of different pH values used as eluents.

This list is by no means exhaustive: there are many other possibilities which could be investigated.

Some Sources of Information

Column capacity

For a strong cation exchanger, add a small known volume (4-5 cm^3) of 0.1 mol l^{-1} NaCl and wash it through with distilled water. Acid will leave the burette (test that it is all through) and can be titrated with 0.1 mol l^{-1} NaOH. The volume of NaOH required will be equal to the volume of NaCl added to the column. Now continue the process by adding further portions of NaCl until the volume of NaOH required is less than expected. At this point the column is saturated with Na^+.

In later experiments 50% of the column capacity should not be exceeded.

The column can be regenerated into the hydrogen form by using an excess of 2 mol l^{-1} HCl to displace the $Na^+(aq)$.

Investigation 1:
"The Determination of Calcium in Dietary Supplement Tablets by Ion-Exchange: A Freshman Laboratory Experiment" by M.L. Dietz, *Journal of Chemical Education*, 1986, **63**, 177

Investigation 3:
"Anion Exvhange Studies VI: The Divalent Transition Elements Manganese to Zinc in Hydrochloric Acid" by K.A. Kraus and G.E. Moore, *Journal of the American Chemical Society*, 1953, **75**, 1460

"Ion-Exchange Chromatogrpahy for High-School Students" by W. Rieman, *Journal of Chemical Education*, 1954, **31**, 215
"Cation Analysis by Ion Exchange for the course of Qualitative Analysis" by J.B. Berend, L.B. Westcott and E.O. Wiig, *Journal of Chemical Education*, 1958, **35**, 68

Investigation 4: *Journal of Chemical Education*, 1990, **47**, 808

General reference on ion exchangers

http://www.remco.com

Ion Exchange -A Special Study, *Nuffield Advanced Science*, Penguin Education

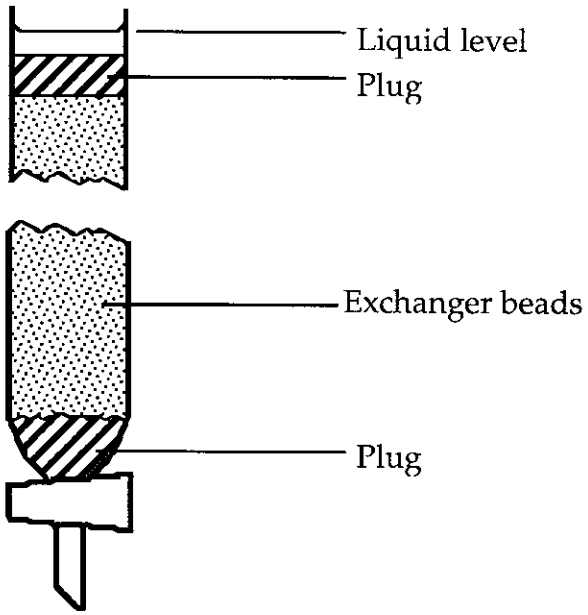
Help and Hints

Preparation of a simple ion exchange column

1. Weigh out about 20 g of the exchanger beads and leave them to soak in water overnight.

2. If a cation exchanger is being used, pour off the water and cover the beads with 2 mol l^{-1} HCl (2 mol l^{-1} NaOH for an anion exchanger). Stir and leave to soak for about 10 minutes. This fills the exchange sites with $H^+(aq)$ or $OH^-(aq)$ as the case may be. Drain off the acid (or base) and repeat the soaking with fresh acid (or base).

3. Place a plug of glass wool at the base of the burette. Pour in the acid and beads as a slurry and allow the beads to settle, making sure that there is about 1 cm depth of liquid above the beads.



4. Run distilled water through the column to wash out the excess acid until there is no acid reaction to indicator paper from a drop. The beads must never be allowed to become dry. To ensure this there must always be a minimum of 1 cm of liquid above the level of the beads.

5. If air bubbles are trapped in the column the exchange will be inefficient. Air bubbles can be removed by gentle back washing which can be achieved by attaching a piece of rubber tubing to the water tap and filling it with water. The tube is then attached to the jet at the foot of the column and a very slow stream of water allowed to work its way up through the column displacing the bubbles. Tapping the column with a finger will help too.

The column is now ready for exchange. It would be wise, however, to check on the capacity of the column so that it is never overloaded in later experiments.

Optical Activity

Investigation Brief

Optical activity is one of the most fascinating properties that a molecule can exhibit. Molecules which are optically active are said to be chiral, and many chemical reactions in biological systems are affected by chirality.

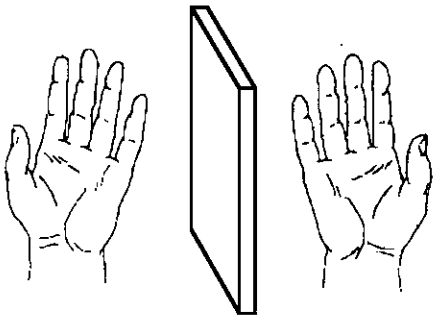
The easiest way to consider chirality is to think of objects in pairs. If the two pencils are placed tip to tip, one pencil is the mirror image of the other.

However, by rotating one pencil, it is possible to superimpose or 'fit' one pencil on top of the other.

A pencil is considered to be a **non-chiral** object because the two can be superimposed exactly.

A pair of objects which cannot be made to match edge for edge, corner for corner, but which are related through being mirror images are non-superimposable and are said to be a **chiral pair**.

Chiral pairs exist in the human body, with hands being the most obvious example.

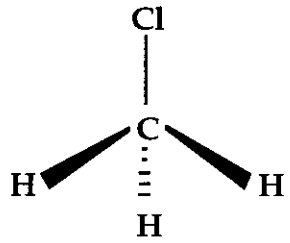


mirror

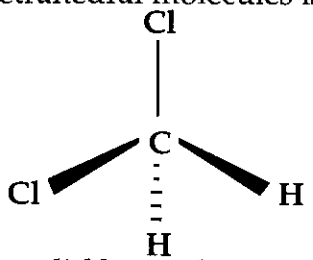
If you make palm coincide with palm, thumb with thumb etc., you have the backs facing away from each other. The **image** of your left hand in a mirror looks the same as your right hand. However, you cannot superimpose one hand on to the other - the fingers will not match. Left and right hands are a chiral pair. We become aware of this when we try to pull gloves onto the wrong hands!

A similar situation applies to molecules with a tetrahedral shape. However, not all tetrahedral molecules are chiral. For example, a methane molecule (CH_4) is not chiral because all the corners are the same and so can be superimposed.

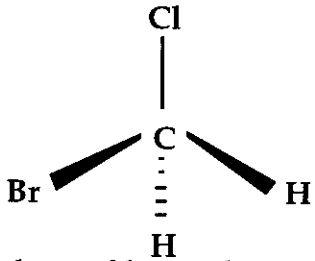
Equally, none of the following tetrahedral molecules is chiral.



chloromethane

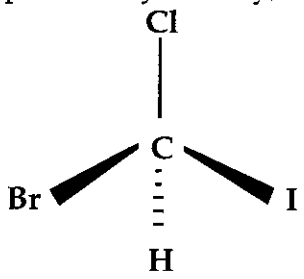


dichloromethane



bromochloromethane

In a chiral compound there is no plane of symmetry, as in this molecule.



bromochloroiodomethane

The mirror image of this molecule cannot be superimposed on to itself. The two different, non-superimposable versions of chiral molecules are called **optical isomers**.

In general, for an object to be chiral it can't have a plane of symmetry. If the object does have a plane of symmetry then it is said to be **achiral** (or **non-chiral**).

It is always the case that a carbon atom with four different groups attached is chiral. To understand the concepts, it really is essential that you make models of the molecules. Try using a mirror too!

The study of chirality using polarized light

Light from normal sources is unpolarized; that is, the electric and magnetic field vectors are orientated in random directions about the axis of the light beam.

Polarized light can be produced in a variety of ways, but the simplest and cheapest method is to use 'Polaroid' filters made of a synthetic material that only transmits light polarized in one direction.

Placing a sheet of 'Polaroid' filter in front of a lamp results in most of the light being absorbed. Only light polarized along the axis of the filter is transmitted. If a second sheet of filter is placed on top of the first, theoretically no light will be transmitted unless the axes of the two filters are parallel.

If an optically active (**chiral**) substance is placed between the two filters, the molecules interact with the light and rotate its axis of polarization and the second filter has to be rotated by a certain angle in order to see the light again. This is the basic principle of a **polarimeter**.

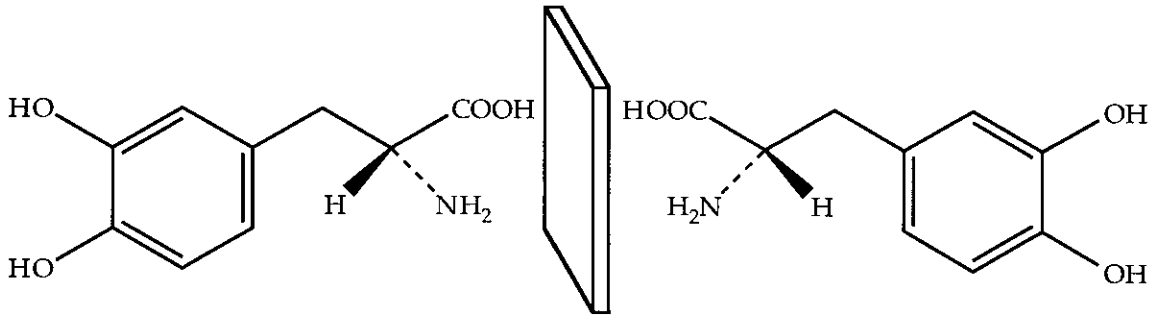
When polarized light (light polarized along a particular plane or axis) passes through certain media there is a rotation of the plane of polarization which may be measured quantitatively using a polarimeter. The direction or sign of rotation will depend on the

particular substance and pairs of chiral isomers will show optical rotation of the same magnitude but opposite sign.

In most biological systems only one isomer is present; however if there is a mixture of isomers present in equal amounts the mixture is optically inactive because the rotation of polarised light by one isomer is exactly cancelled by the rotation from the other isomer. This mixture is described as a **racemic mixture**.

Chirality in Nature

It is usually the case that optically active isomers will possess different biological properties. An example of this in nature is the amino acid Dopa, which is 2-amino-3(3,4-dihydroxyphenyl)propanoic acid. It exists in two forms. D-Dopa has no physiological effects on humans whereas the other isomer, L-Dopa, is widely used in the treatment of Parkinson's disease, a disease which attacks the central nervous system.



D-Dopa
(no biological effects)

mirror

L-Dopa
(Parkinson's treatment)

The reason for this dramatic difference is the ability of L-Dopa to fit into a chiral receptor site, in the same way that a left hand fits into a left glove. The other isomer D-Dopa doesn't fit the receptor site, just as a right hand won't fit into a left glove.

Many modern medicines are chiral molecules and usually are present in the pure form of one isomer or the other. This is a result of the case of thalidomide which was given to expectant mothers during pregnancy as an anti-depressant. Unfortunately the drug was a racemic mixture and the isomer which had no effect as an anti-depressant caused damaging effects on unborn babies. If this isomer had been removed, the drug would not have caused the birth defects.

It is important to realise that optical activity is not a property of compounds restricted to organic chemistry. Many inorganic compounds can exist as optically active isomers and this was originally used in studies of the coordination of transition metal complexes to demonstrate the existence of octahedral geometry in some complexes. Also, different minerals have different optical activities - thin sections of rock are examined using polarized light in a microscope. This helps in the identification of the constituent minerals.

Some Starter Questions

- Why is "chirality" so important?
- Are all molecules "optically active"?
- What makes a molecule optically active?
- Can chiral molecules be easily identified?
- Do isomers of the same molecule exhibit the same optical activity?
- Is it possible to show some molecules have different optical activities?
- Are there any examples where optically active isomers are used?
- How could you detect the ability of molecules to rotate the axis of polarization?
- What is a "racemic mix"?
- Why does a racemic mixture show no optical activity?
- Is it possible to separate the isomers in a racemic mix?
- Are there any problems associated with racemic mixes?
- What does the notation "D" and "L" mean in the context of isomers? What about + and - in the context of D(+) glucose?
- How can transition metal complexes show chirality?
- What is "octahedral geometry"? What makes this geometry chiral?

These are only some of the questions that could be asked. If you can think of others, please do so.

Possible Investigations

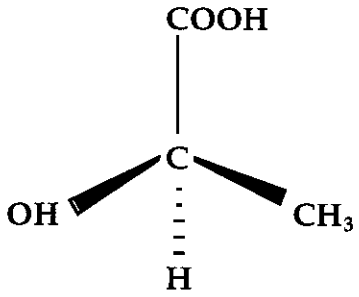
1. The angle of rotation (α) depends on:
   (a) the nature of the substance,
   (b) the length of the sample through which light passes,
   (c) the concentration of substance in solution,
   (d) the wavelength of light used,
   (e) the temperature of the sample.
   Investigate how α changes with some of these factors. Which has the greatest effect on α? Which has the least effect on α?

2. Determination of the rotation of sugars and other organic compounds and hence the concentration of solutions.

3. Investigation of the kinetics of 'sugar rotations' using a disaccharide as the reactant.

4. Investigation into the activity of micro-organisms, e.g. ***penicillium glaucum*** , which feed on one particular form of the racemic mix of tartaric acids leaving the other behind. The optically inactive mixture thus becomes progressively more active.

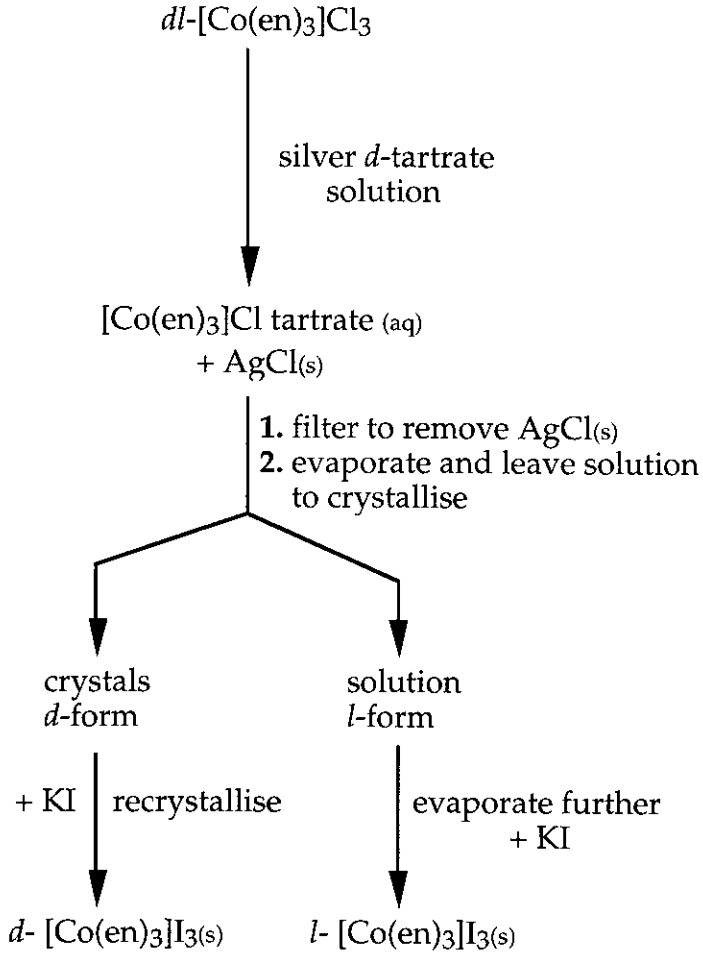
   Most of biochemistry is controlled by the chirality of molecules.
   Consider, for example, lactic acid ($CH_3CHOHCOOH$).



   Try drawing the other isomer, referring back to the earlier page. (Remember that a compound with a carbon carrying 4 **different** substituents is chiral.) Make models of both and compare them.

   The (+) form is found in muscle tissue whereas the (-) form is found in sour milk. The (+) form is produced in muscles during exercise when the cells switch from aerobic to anaerobic respiration. The lactic acid accumulates as a waste product and causes the sensation of muscle fatigue, but it is gradually carried away by the blood to the liver. The liver cells convert lactic acid to pyruvic acid, but this process requires oxygen. As a result, anaerobic respiration in muscle cells produces an 'oxygen debt' that is paid back from inhaled oxygen after exercise has ceased.

5. Making inorganic octahedral chiral isomers. An example involves the complete resolution of the tris-ethylenediamine complex of cobalt (III). This process makes use of naturally occurring *d*-tartaric acid to separate the isomers.
The two isomers can be separated as follows:



6. Growth and separation of large crystals of racemic tartaric acid into right and left handed forms by repeating experiments done by Louis Pasteur.

   A racemic mix consists of both right and left handed forms of the compound in equal proportions. This is not optically active. It is possible by observation to see differences between the faces of the crystals of the two forms and, as a result, it is possible to separate them physically into the two forms with the aid of a magnifying glass. The efficiency of the separation technique can be checked by dissolving the two sets of crystals separately in water and then measuring the optical activity using a polarimeter.

This list is by no means exhaustive: there are many other possibilities which could be investigated.

Some Sources of Information

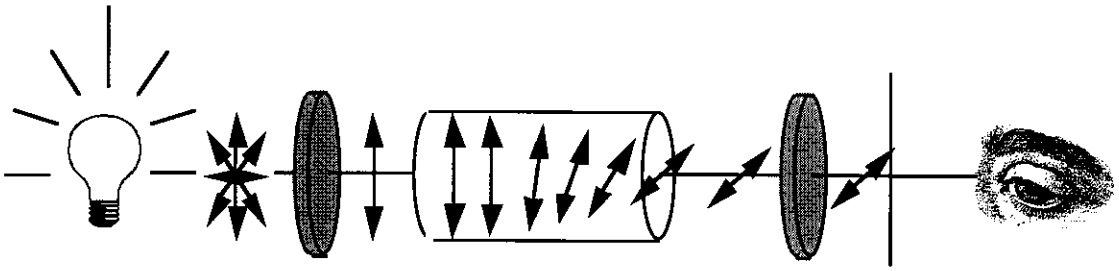
Investigations 1 and 2:

Descour L, *Pasteur and His Work*, T.F.Unwin, London, 1922

"An Easily Constructed Student Polarimeter" by R. Shavitz, *Journal of Chemical Education*, 1978, **55**, 682

The polarimeter

In a polarimeter, the monochromatic light from a sodium vapour lamp is passed through a 'Polaroid' filter, and the polarized light passed through the sample contained in a glass tube. The light then passes through a second 'Polaroid' filter, fitted on a rotating mount, and is viewed through an eyepiece.



Light Source | Polarizer | Sample tube containing chiral molecules | Analyser | Observer

The analyser and polarizer are rotated so they are at right angles, where **maximum darkness** is obtained. This is taken as the zero position. With a solution of a chiral compound between them, the analyser has to be turned until maximum darkness is obtained again giving a measure of rotation. With two optical isomers of the same material, one will rotate in one direction while the other will rotate equally in the opposite direction.

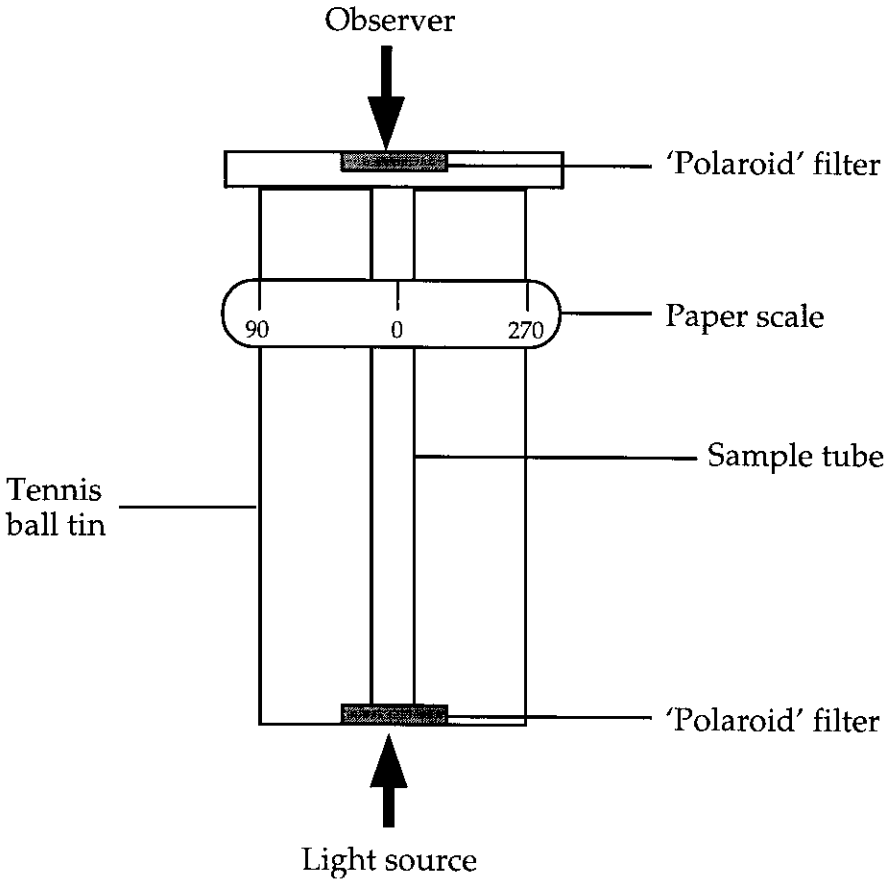
Help and Hints

Simple polarimeter

A simple polarimeter can be constructed from a long cylindrical container such as a tennis ball tin.

Having removed the bottom, a Polaroid filter is placed in the middle of a sheet of card and this is then taped to the bottom of the container. The other Polaroid is fitted to the plastic top. A strip of paper is wound round the outside of the container and marked off in degrees to form a scale.

The sample tube is sealed if necessary and placed in the container between the two Polaroid filters. It may be necessary to add some packing around the sample tube to keep the tube in place and to allow all the light from the lamp to pass from one filter through the sample to the other filter. The plastic top is then turned until maximum darkness is obtained, giving a measure of the optical rotation.



A white light source can be used, but it produces unwanted colour effects which can be avoided by using a monochromatic source such as a sodium vapour lamp.

Paramagnatism

Investigation Brief

Magnetic properties have been observed and used for centuries and are of vital importance in modern technology. The magnetic behaviour of a material can also reveal much about the electronic structure of the atoms in that material.

There are three different types of magnetism:

Ferromagnetism
This is the most commonly met form as it is used in 'magnets' like fridge magnets. Each magnetic object has two opposite 'poles' called north and south. Really these poles should be called 'north-seeking' and 'south-seeking' as the Earth is really a giant magnet in this sense and poles of a magnet point toward the North (magnetic) Pole and the South (magnetic) Pole of the Earth respectively. Like poles repel, unlike poles attract. Iron, cobalt and nickel are the three magnetic elements but some metal oxides also exhibit this property. One (magnetic iron oxide) was the first to be used in compasses, by the Chinese.

Paramagnetism
Although this is much weaker than ferromagnetism, it is strong enough to be measured in the lab with relatively simple equipment. Paramagnetism is associated with unpaired electrons and a paramagnetic substance will be attracted toward and into a magnetic field rather than toward a magnetic pole.

Diamagnetism
This is much weaker than paramagnetism and cannot be easily detected, despite being present in all matter. It is associated with paired electrons. Diamagnetic substances are repelled (very weakly) from a magnetic field.

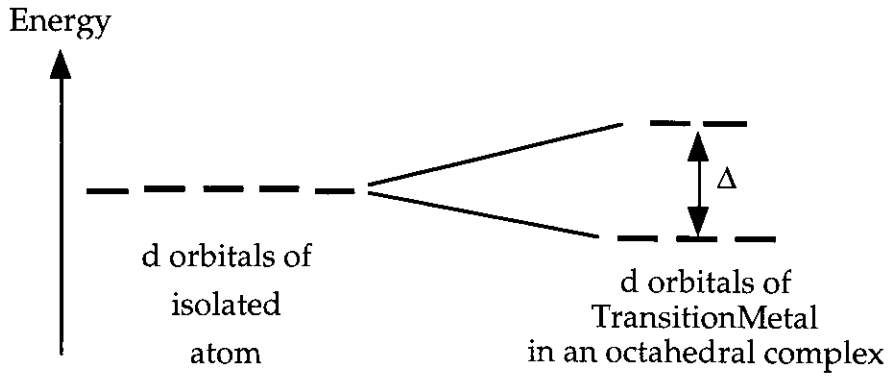
Electrons can behave like little magnets due to their spin – they can be thought of as spinning in one of two directions. Just as an electric current moving round a coil of wire produces an electromagnet, so an electron rotating creates a magnetic field which can be in one of two directions depending on the direction of rotation.

When there are two electrons occupying an orbital in an atom their spins align in opposite directions ('pair off') and the two magnetic fields cancel each other out. If there is only one unpaired electron in an atomic orbital then its magnetic field is not cancelled out and can be measured.

If atoms with unpaired electrons are placed close to a magnetic field, such as a large horseshoe magnet, then those unpaired electrons are attracted towards that magnetic field. The magnitude of the attraction is related to the number of unpaired electrons in the compound and the strength of the magnetic field.

Many transition metal compounds are paramagnetic due to the arrangement of electrons in the five d-orbitals round the metals. Although all five d-orbitals have the same energy in an isolated atom, some gain and some lose energy when forming complexes. Common shapes include octahedral, square planar and tetrahedral.

For octahedral complexes, the d-orbitals split into two sets as shown opening up an energy gap between them called Δ (delta). The magnitude of the gap depends upon the ligands involved.



For transition metal ions with 1, 2, 3, 8, 9 or 10 electrons such as Cr^{3+} (a d^3 species), there is only one possible arrangement of the electrons with, in this case, all three d-electrons unpaired and with parallel spins and in the lower set of orbitals.

When there are between 4 and 7 d-electrons present, there are two possible arrangements:

- one with as many unpaired electrons as possible, called high spin
- the other with as few unpaired electrons as possible, called low spin.
- The half arrows represent electrons below:

a high-spin d^4 species

a low-spin d^4 species

Which arrangement is adopted depends on the magnitude of Δ and the energy required to pair off electrons in an orbital. If Δ is larger than the energy required to pair electrons, then the low spin arrangement is adopted; conversely, if the pairing energy is greater than Δ, a high spin arrangement is observed.

High spin and low spin complexes have different numbers of unpaired electrons and so have different paramagnetic behaviour. This can be used to determine which arrangement is present in a transition metal complex.

Transition metals in different oxidation states also have different arrangements of electrons and so can have differing numbers of unpaired electrons. For example, manganese has a variety of oxidation states, including Mn(VII) in potassium permanganate, Mn(IV) in manganese dioxide and Mn(II) in manganese(II) sulphate. Each of these has a different number of unpaired electrons and so a different degree of paramagnetism.

Some Starter Questions

- What is meant by "electron spin"?
- How does this relate to the three types of magnetism mentioned?
- Why do electrons pair in an orbital so that their spins cancel?
- Can more than two electrons be found in a single orbital?
- How is the number of unpaired electrons related to the effect of a magnetic field on a paramagnetic compound?
- How strong a magnetic field is required to see paramagnetic effects?
- What are "d-orbitals"?
- What are "octahedral, square planar and tetrahedral" complexes?
- What is a "ligand"?
- What are the "high-spin" and "low-spin" configurations of a transition metal?
- What is the "pairing energy" for electrons?
- How does Δ change with different ligands?
- How does the electronic arrangement affect the colour of a compound?

These are only some of the questions that could be asked. If you can think of others, please do so.

Possible Investigations

1. Compare the magnetic properties of a known series of solid compounds such as $KMnO_4$, MnO_2 and $MnSO_4$. Think carefully about the amount of each substance that should be used.

2. Does it make any difference if the substances are in solution?

3. Look at what transition metal compounds are available. Choose one metal.

- Can other complexes of that metal with different oxidation states be synthesised?
- Can complexes of the metal with the same oxidation state but different ligands be synthesised?
- What happens if the same ligand is used and the metal varied?

In each case, their paramagnetic properties could be measured and compared to theory.

Another substantial part of the investigation could be devising, constructing and testing a suitable experimental set up.

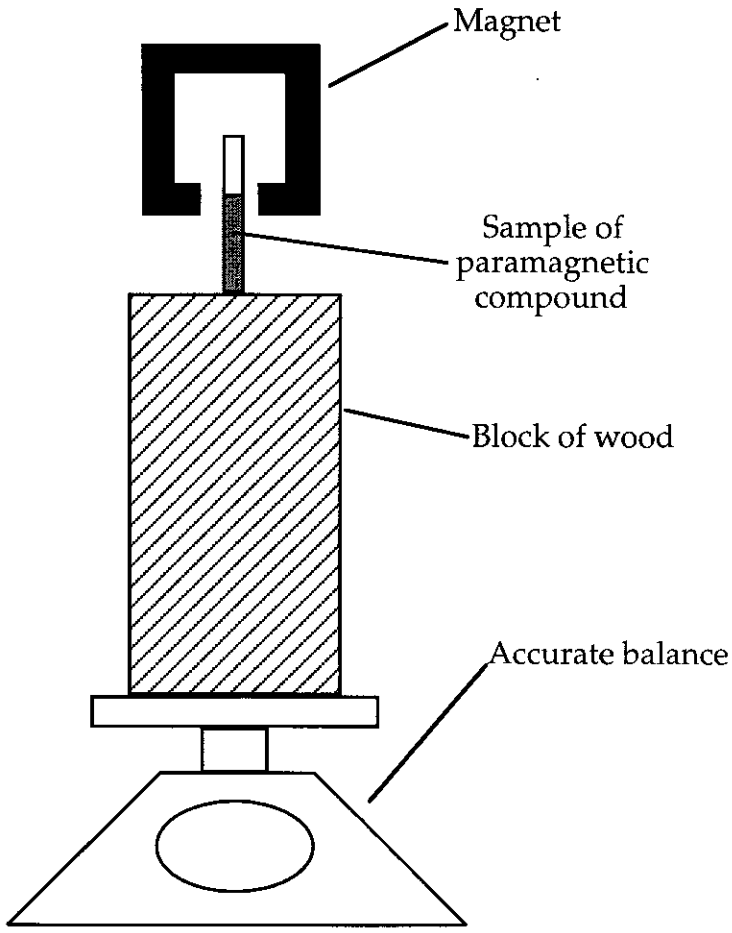
This list is by no means exhaustive: there are many other possibilities which could be undertaken.

Help and Hints

Although paramagnetism is not as strong an effect as ferromagnetism, it can be detected fairly easily using simple apparatus. Two possible designs are given below.

In both cases, the strength of the magnet is crucial. In one school, the teacher found a large horseshoe magnet from the school Physics Departments which worked well. The teacher then purchased one for Chemistry!

1.



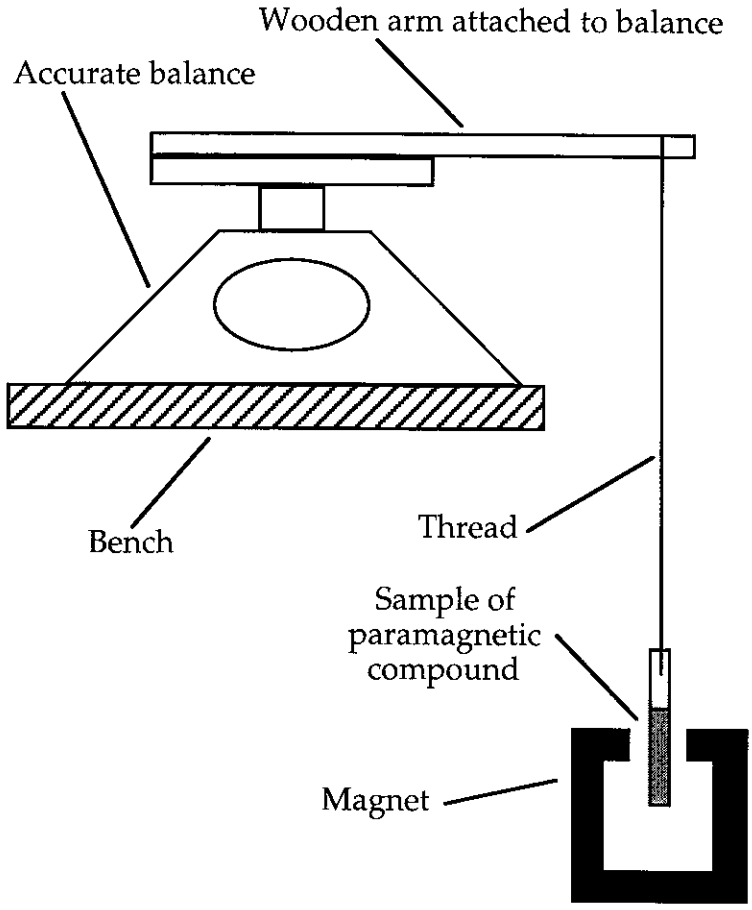
The sample to be tested is placed in a test tube on a wooden block, tall enough to keep the magnet far enough away from the balance so as not to affect it. The balance should be accurate to at least three decimal places.

The magnet is gently lowered toward the sample which is attracted into the magnetic field, with the balance reading decreasing accordingly. This is done repeatedly and the maximum affect (that persists for half a second or so) is recorded.

The more unpaired electrons in the sample the stronger the effect and the more mass the sample will appear to lose. The samples can be put in order of paramagnetic strength, or of the number of unpaired electrons they have. (NB - The relationship between the two is not necessarily linear.)

2. The same technique can be used with a slightly different set up, where the mass of the sample will appear to increase in the presence of a magnetic field.

An old analytical balance has been used with success with the light wooden arm attached to the beam and a hole cut in the glass case for it to protrude.



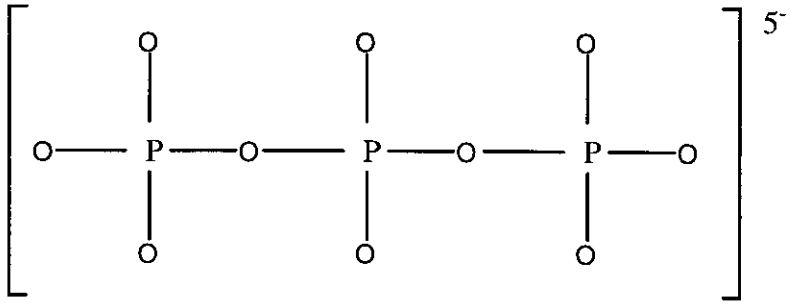
Phosphates in Washing Powders

Investigation Brief

Modern detergents are not made up only of surfactants, but contain a variety of materials such as builders, fluorescers and bleaches. Phosphates are used as builders - they have three functions which assist in the work of the surfactants.

- They act as buffers to keep the washing solution from having too high a pH which can damage fabrics.
- They act as sequestering agents which form complexes with ions in hard water (Ca^{2+}, Mg^{2+}) and keep them from reacting with the surfactant. (Soaps with hard water produce scum).
- They help to keep clay-like dirt in suspension so that it is not redeposited on the material being washed.

The common phosphate found in washing materials is the tripolyphosphate (the pentasodium salt)



This can hydrolyse to the orthophosphate $(PO_4)^{3-}$ which can be troublesome in the environment.

To determine the amount of phosphate in a detergent, it is convenient to convert the tripolyphosphate into orthophosphate and then measure it photometrically through its coloured complexes with transition metal ions.

The hydrolysis is carried out at about pH 1 at temperatures between 90-100°C.

The complex is formed between the PO_4^{3-} and a mixture of ammonium vanadate (NH_4VO_3) and ammonium molybdate [$(NH_4)_6Mo_7O_{24}.4H_2O$]. The yellow colour which develops is compared photometrically with phosphate solutions of known concentration treated similarly.

Some Starter Questions

- What are "surfactants", "builders", "bleaches" and "fluorescers"?
- How do the surfactants affect the detergents?
- Why are "builders" added to detergents?
- Why are "fluorescers" added to detergents?
- Why are "bleaches" added to detergents?
- What is a "buffer" and how do phosphates act as buffers in detergents?
- What is a "sequestering agent"?
- How do phosphates keep clay-like dirt in suspensions?
- Why is orthophosphate troublesome in the environment?
- What is meant by "measuring the amount of phosphate photometrically"? How could this be done?
- Why is the hydrolysis carried out at around pH 1?
- Why does the temperature have to be between 90-100°C?

These are only some of the questions that could be asked. If you can think of others, please do so.

Possible Investigations

1. Determination of phosphate in a range of detergents.

2. Compare the results with those from shampoos, dishwasher cleaner etc.

3. Determination of phosphate in river waters at various points on a river from source to mouth and just below tributaries.

   - How do the results relate to land use (e.g. type of farming)?
   - How do the results relate to local industries?
   - How do the results relate to bus cleaning depots?
   - How do the results relate to car wash centres?
   - How do the results relate to sewage treatment plants?

4. Relate river or loch phosphate concentrations to species of living organisms in the water.

5. Compare phosphate concentrations in the same brand of detergent bought in different areas and relate this to the hardness of the water in those areas.

This list is by no means exhaustive: there are many other possibilities which could be investigated.

Some Sources of Information

"An Introductory Experiment on Phosphates in Detergents" by J.R.Mohrig, *Journal of Chemical Education,* 1972, **49**, 15.

This starter investigation could also be linked to the Starter Investigations dealing with Detergents and Testing the Water.

Identification of an Unknown

Investigation Brief

The ability to identify an unknown compound is obviously very important in chemistry. For example, if the structure of a naturally occurring drug is known, then attempts can be made to produce it synthetically or to improve its therapeutic properties by modifying the molecule. Similarly, identifying impurities in chemical products is of vital importance.

There is a long tradition of analytical techniques in chemistry, based on using characteristic chemical reactions and physical properties to identify organic compounds. These techniques are still used today, but have been complemented by modern ones based on different kinds of spectroscopy which can yield information about chemical structures quickly and easily from small samples.

Organic compounds are classified according to the functional groups present in them. As these groups will determine the kind of reactions that the compound will undergo, then such reactions can be used to confirm the presence of particular functional groups in an unknown compound.

Standard tests for identifying ketones, aldehydes, amines and most other common functional groups are well documented. However, functional group tests are unlikely to be able to identify a compound uniquely on their own.

Physical properties, such as melting point, can also be used to help identify unknown compounds by comparing them to samples of known identity.

Most pure crystalline solids melt over a characteristic temperature range (e.g. melting began at 103°C and was over by 105°C). The higher the sample's purity, the smaller this range. Once the identity of a compound has been narrowed down, a mixed melting point can be used to prove its identity. If equal amounts of two compounds are mixed together and their melting point taken, there are two possible outcomes:

- if the two are the same, there will be no difference in the melting point of the mixture and that of the two components separately;
- If the two are different, the mixture will melt at a lower temperature and over a wider range than expected.

Producing a solid derivative of a compound, determining its melting point and consulting data tables is another common technique used to help confirm identity.

Dissolving an unknown compound in a solvent can alter the freezing point of that solvent (this is why salt is put on roads to help melt ice in winter). The extent of this depression is related to the number of particles of the unknown compound in solution and to its molecular mass. Camphor is often used as a solvent and the depression of its freezing point measured to calculate the molar mass of an unknown solute. This is an example of a **colligative property**.

Another useful physical property that can be used to separate compounds from a mixture and/or identify them by comparison to known samples is the polarity of the

compound, which depends on the kinds of bonds in the molecule and its size. Chromatography can use this property.

Chromatography is a process which can determine how many components are present in a sample and can allow their identification by comparison with authentic samples. There are many different kind of chromatography which all work in essentially the same way.

Spectroscopy has transformed modern chemistry techniques since the middle of the 20th Century. Three such techniques are infrared, mass and nuclear magnetic resonance (NMR) spectroscopy.

Infrared spectroscopy uses the movements of atoms within bonds to gain information about functional groups. Chemical bonds are not rigid - the atoms are in constant motion, such as stretching and bending and the energy corresponding to this motion lies within the infrared portion of the electromagnetic spectrum. An infrared spectrum of a compound shows peaks corresponding to its functional groups present at different characteristic wavelengths. If a spectrum has that particular peak, then the functional group can be identified from standard tables of data.

Mass spectrometry gives information about the formula and structure of a compound. Samples are turned into ions (in a gas state) which are then separated according to their mass to charge ratio (m/z - where m is the mass of the ion and z its charge). Sufficiently high ionisation energies can breaks the molecule into fragments, which are also detected and can often be identified. This can help decide the structure of the compound using the same sort of thought processes as are used to do a jigsaw.

NMR is another technique which allows chemists to examine the structure of a compound without destroying it. Some atomic nuclei have spin, in a similar way that electrons have spin, and, just like electrons, their spinning charges produce a small magnetic field. The interaction between these nuclear magnets and an applied magnetic field can be detected in an NMR spectrum. The nuclear magnets have different strengths depending on where in a molecule they are and the other atoms nearby (or more importantly their electrons). Each magnetically different part of the compound is called an **environment**. The number of environments and the number of magnetic nuclei in each can be determined in this way. The patterns generated in the NMR spectrum give information about which environments are next to which, and so can be used to work out which atoms (or groups of atoms) are next to which. Fortunately nuclei of the most common isotope of hydrogen exhibit this property and so be used to produce an NMR spectrum of organic compounds, often called a ^{1}H (proton) spectrum.

Note for teachers

Compounds with one or two functional groups, perhaps with an aromatic ring, are suggested. You will probably have suitable compounds from a local company, college, or university. Pupils should be informed of any special safety hazards but, in any case, they should treat unknowns as hazardous.

Some Starter Questions

- What are the tests for common functional groups?
- How can they be used to help identify an unknown compound?
- What are "physical properties"?
- How can melting point be measured?
- What is a "solid derivative"? Why are they used?
- How can the depression of freezing point be related to molecular mass?
  How can depression of freezing point be measured?
  Why is camphor often used as a solvent in this measurement?
- What are colligative properties? Name some other colligative properties.
  How can they be measured?
- What is chromatography?
  How does it work?
  What different types of chromatography are there?
- How do infrared, mass and NMR spectroscopy work?
  How can they be used to help identify an unknown compound?

These are only some of the questions that could be asked. If you can think of others, please do so.

Possible Investigations

From the title, there is apparently only one possible investigation from this Starter Investigation. There are of course many compounds that could be used; they need not be organic and mixtures could be given (as long as the pupil is told this).

However, there are a variety of possible ways to tackle the investigation. Probably the most useful is to carry out a variety of chemical and physical tests in the lab to see how much can be discovered this way. Only when a possible structure (or structures) has emerged should it be verified by spectroscopy, perhaps carried out at a local company or University.

Some Sources of Information

A wide range of standard chemical tests are available to detect the presence of a variety of functional groups. Some of them may well be familiar, but others can be found readily from textbooks that set out standard experimental procedures.

Other useful references are:

D.H. Williams and I. Fleming, "Spectroscopic Methods in Organic Chemistry"

"A Simple and Effective Method for Melting-Point Determination" by T.M. Brown and A.T. Dronsfield, *School Science Review*, 1990, **72**, 110

Chromatography

Although there are several kinds of chromatography, thin-layer chromatography is one that is particularly useful in identifying compounds by comparison with known samples.

For thin-layer chromatography (TLC), a glass plate, such as a microscope slide, is coated with a thin layer of very finely ground silica (SiO_2) or cellulose suspended in water or other solvent. If a spot of a solution of a compound is applied to the plate and the solvent allowed to evaporate, the compound will be adsorbed onto the surface of the plate.

If an eluent (the name given to the solvent in chromatography) of low polarity is allowed to travel along the silica coated plate, the compound has the choice of staying adsorbed or of dissolving in the eluent. If the compound is non-polar, it will dissolve and be carried along in the moving eluent. A compound in solution is being constantly exposed to fresh silica and so may be readsorbed. Equally, an adsorbed compound is being exposed to fresh eluent moving up the plate and may dissolve. Any one molecule will be constantly stepping on and off the "conveyer belt" of moving eluent. Non-polar molecules will spend most of their time in solution, and so will be carried rapidly up the plate; polar molecules will spend most of their time adsorbed, and their movement will be slow compared to the eluent. As polar and non-polar molecules move at different rates, we have a method of separating and identifying them.

Each compound can be characterised by a measurement of how far the spot has moved relative to the eluent front.

$$R_f = \frac{\text{distance moved by spot}}{\text{distance moved by eluent front}}$$

R_f values are fixed for a given compound on a given stationary phase and with a particular eluent.

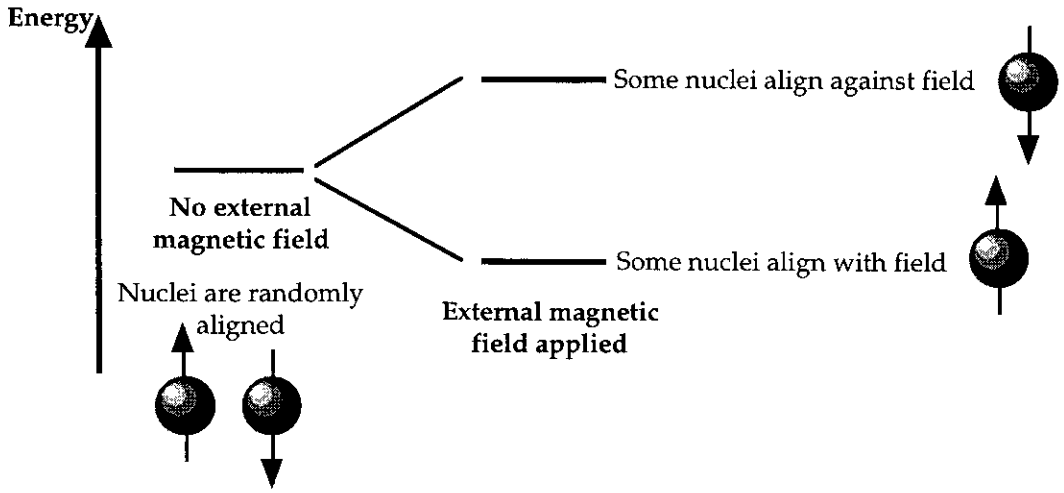
Identity checks can be made using a pure sample of the compound. If the sample of pure compound and the sample of the unknown are run side by side on the same plate and they have different R_f values, then they are different compounds. If their R_f values are the same, they may be the same compound.

If the eluent is changed and the two substances still have the same R_f value, it is increasingly likely that they are the same substance.

Spectroscopy

NMR Spectroscopy

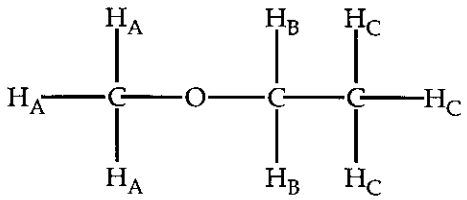
If the spins of the protons and neutrons in a particular atomic nucleus are not paired then the atomic nucleus has spin, I, and this movement of charge makes them act like little magnets. Normally these nuclei are orientated in a random fashion, but in a strong magnetic field they align themselves in that field in 2I+1 ways. So for a nucleus like ^1H, which has $I=^1/_2$, there are two ways of alignment, either with the field or against it, and these will have different energy levels.



When a radio signal of the right frequency is applied to these nuclei, the number in the upper energy level increases. The frequency at which this happens depends on the applied external field and the nuclei involved. It is transitions between these energy levels that are detected in an NMR spectrum.

Each ^1H nucleus in a molecule is surrounded by electrons and (usually) other nuclei which can also behave as magnets and will affect the ^1H nucleus and the net magnetic field it experiences in NMR spectroscopy. Nuclei which have the same atoms or groups of atoms around them are said to be in the same **chemical environment**. Each environment experiences a different net magnetic field and so absorbs radio signals at a different frequency.

Consider the following ether, methoxyethane:

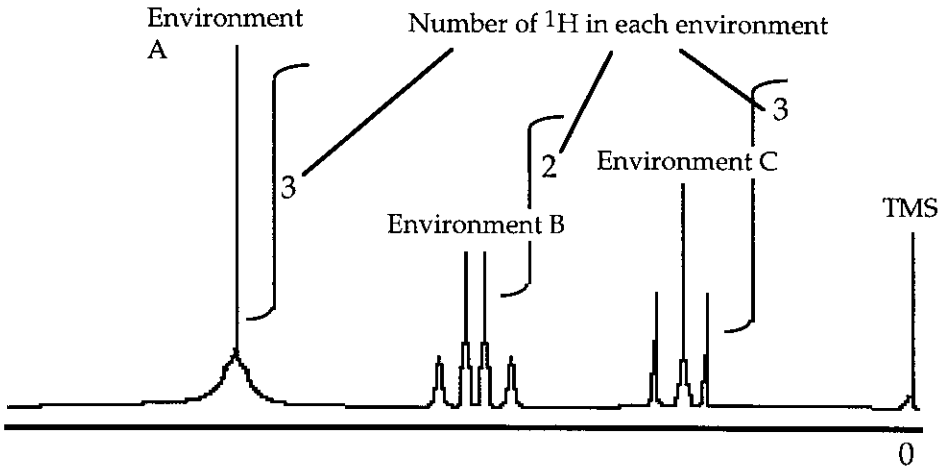


It has three different ^1H environments (which we shall call A, B and C). Environment A has a $-CH_3$ group, directly attached to an O; environment B is a $-CH_2-$ group with an $-OCH_3$ on one side and a $-CH_3$ on the other; environment C is a $-CH_3$ group attached to a $-CH_2-$ group. Each of these environments will be detected in an NMR spectrum and so three different environments will show on the spectrum. Environments which are close to electron withdrawing groups (such as environment A) experience stronger net magnetic fields than those further away, and are said to be **deshielded**. The strengths of the magnetic fields at different environments are measured relative to a standard of tetramethylsilane (TMS), which is given a value of zero. NMR spectra are given on a scale called the chemical shift (δ). The more deshielded a nuclei is the greater is its chemical shift. In this case, environment A has the highest chemical shift because it is next to the electronegative O atom, environment B has the next highest and environment C (furthest away from the O) has the lowest.

The areas of the peaks on an ^1H NMR spectrum are related to the relative number of ^1H nuclei present in each environment. So for methoxyethane, the spectrum shows the peak at the highest chemical shift corresponding to three ^1H, the next highest to two ^1H and the peak with the lowest chemical shift would correspond to three ^1H. The ratio of the number of ^1H in each environment is then 3:2:3.

Normally the peaks on a ^1H NMR spectrum are split into doublets, triplets, quartets, or even more complex patterns depending in the number of ^1H atoms next to a group. The splitting is caused by interactions between neighbouring atoms which have spin (such as other ^1H atoms) and the number of splits is equal to the number of neighbouring hydrogen atoms + 1. So in the example above the peak corresponding to environment A is a single peak as there are no ^1H on the neighbouring atom, the peak for environment B is split into a quartet (3 ^1H 'next door' + 1) and the peak for environment C is split into a triplet (2 ^1H 'next door' + 1).

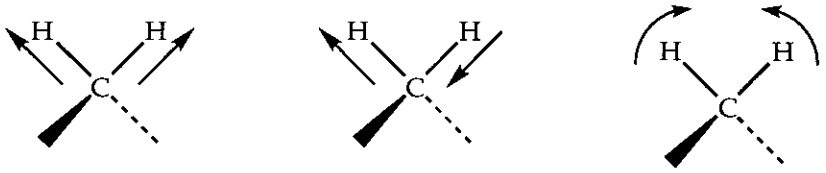
Here is a diagrammatic representation of the spectrum for methoxyethane:



Chemical Shift (δ)

Infrared Spectroscopy

Atoms in molecules are not stationary - they are constantly in motion and the energy associated with that motion corresponds to the infrared region of the electromagnetic spectrum for most vibrations. Relevant vibrations here are stretching and bending:



Symmetric stretch | Asymmetric stretch | Bending

Functional groups have characteristic vibrations which can be detected using infrared spectroscopy.

Only when a particular vibration gives a change in a molecule's dipole moment is infrared radiation absorbed. The particular frequencies of the absorbtion can be used to identify the functional groups present. For historical reasons, the frequency is normally quoted in wavenumbers (cm^{-1}), which is directly proportional to the energy associated with that absorbtion. The usual range of an infrared spectrum is from around 600 cm^{-1} to 4000 cm^{-1}

$$\text{Wavenumber} = \frac{1}{\text{wavelength of light (cm)}}$$

Tables of the characteristic frequencies for many common functional groups are readily available and can be used to identify the peaks on an infrared spectrum.

Help and Hints

Melting point and mixed melting point

Method

Seal one end of a glass melting-point capillary tube by placing it into the edge of a flame and rotating it until the end just collapses and seals. Use a spatula to grind a small amount of the compound on a watch glass (or compounds for a mixed melting point) to a fine powder. Introduce some of this powder into the capillary tube, and ease it to the bottom by tapping the end of the tube on a metal or formica surface. Use this sample to obtain a melting point.
(See "A Simple and Effective Method for Melting-Point Determination" by T.M. Brown and A.T. Dronsfield, *School Science Review*, 1990, **72**, 110 for a suitable apparatus for measuring melting points.)

Infrared spectroscopy

Infrared spectroscopy may be available at a local company or place of higher education.

The infrared spectrum will help confirm the functional groups found by normal analysis. For example:
— OH groups absorb infrared at about 3500 cm^{-1}, while
— C = O groups absorb at about 1700 cm^{-1}.
As well as checking the main groups, check the **fingerprint area**, below 1000 cm^{-1}. This area is unique for each compound; libraries of standard IR spectra are available.

The unknown compound is mounted in the spectrophotometer between two sodium chloride plates (Why not glass plates?):

- If the compound is a liquid, it must be absolutely dry before taking it to the college or company so as not to waste the technician's time. Wet specimens give spurious results with a large –OH absorption showing. The liquid also damages the NaCl plates.

- If the unknown is a solid, it must also be dried and finely ground with a liquid paraffin called nujol before being sandwiched between the NaCl plates.

Some places may incorporate the unknown specimen in a KBr disc before placing it in the spectrophotometer.

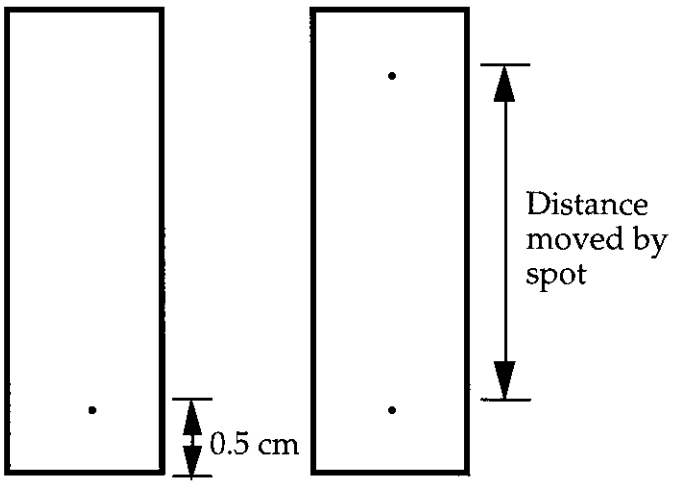
Chromatography

Heat the middle of a capillary tube in a Bunsen flame, remove it from the flame and then pull the ends apart gently. This will cause the capillary tubing to narrow. The tube can be broken at the narrow part to give two fine tubes for making the spots on the silica plate.

Use clean microscope slides to prepare TLC plates. Put two back-to-back and dip them in a slurry of silica gel in the non-polar solvent. Carefully remove the plates, allow them to drip, and then separate them and allow to dry. Commercial alternatives are available.

Dissolve a small quantity of the compound in the solvent (or solvent mixture) being used as an eluent. Use the drawn-out capillary to spot a small amount of solution onto the plate, as indicated below. Use a separate capillary for each substance to avoid contamination.

Stand the plate in a jar containing a little eluent, taking care not to submerge the spot(s), and close the lid. Wait till the eluent has climbed up the plate, then remove the plate and allow to dry. Mark the height reached by the eluent front with a pencil or spatula.

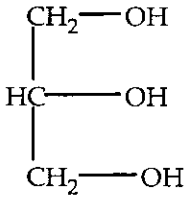


If the compounds are coloured, R_f can measured directly. If this is not the case, the plate is exposed to some iodine crystals in a jar with the lid closed. The iodine is adsorbed where the spots are. On removing the plate from the iodine jar, the spots are marked with a pencil and the R_f value calculated.

Unsaturated Fats and Oils

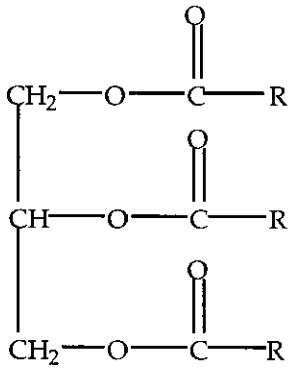
Investigation Brief

Fats and edible oils (not mineral oils) are esters of glycerol (propane-1,2,3-triol).



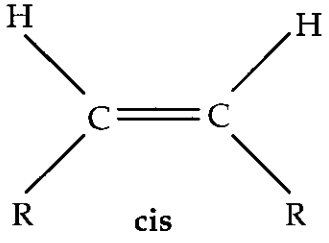
glycerol (propane-1,2,3-triol)

The acid part of the ester consists of three long chain or fatty acids which react with the one molecule of glycerol in a condensation reaction to form the fat or oil. The molecule formed is called a triglyceride.

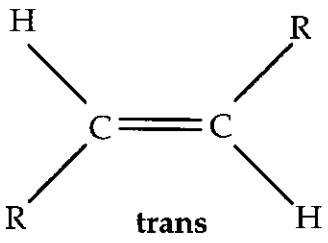


a triglyceride

Where **R** is an alkyl group such as $C_{17}H_{35}$ or $C_{17}H_{33}$. The alkyl groups can be the same or different and can be saturated or unsaturated. The unsaturated groups have a *cis* arrangement round the double bonds rather than a *trans* arrangement.

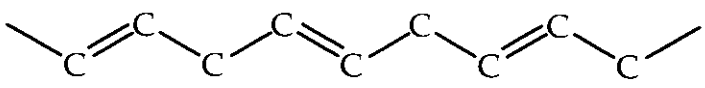


cis



trans

There can be more than one double bond in the fatty acid; if so the double bonds in the chain have two C— C single bonds between the double bonds.

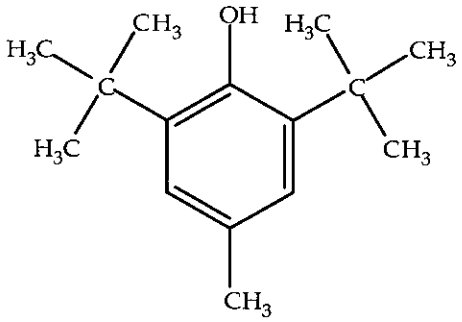


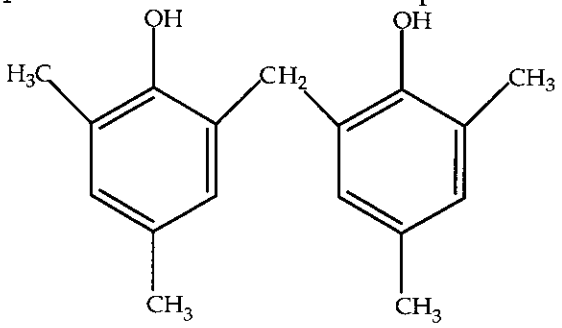
This is unlike conjugated systems in other molecules where the single and double bonds come alternately.

Double bonds in fats and oils are susceptible to attack by oxygen in the air through a free radical mechanism and the result is the production of unpleasant smelling and tasting materials. The fat or oil is said to have become rancid.

A measure of the unsaturation of a fat or oil can be obtained by determining its so-called "peroxide value".

Some oils such as sunflower oil contain naturally occuring antioxidants in the form of Vitamin E. Others like soya and rapeseed require artificial antioxidants to be added to the fats to destroy the free radicals. These compounds are often substituted phenols.





BHT (butylated hydroxytoluene) **E 321** or 2,2 methylene bis (4,6 dimethylphenol)

The oxidation of fats can be accelerated by heating them and at the same time bubbling air through them. From time to time samples can be tested for their peroxide value. Antioxidants can be added and the experiments repeated to find out how effective they are in preventing air oxidation.

When triglycerides are digested, they are hydrolysed to their constituent parts - glycerol and three fatty acids. The stomach is acidic (approx 2 mol l^{-1} HCl) but little breakdown takes place here. However, the contents of the small intestine are strongly alkaline and contain enzymes which speed up the breakdown of triglycerides.

There is no accounting for human taste, however. In some parts of the world such as Mongolia and Tibet, people purposely allow their butter to become rancid and then float it on hot tea and drink it. Cheeses made from the milk of sheep and goats also have a characteristic sharp taste and smell which arises from the oxidation of the unsaturated acids in their fats.

Some Starter Questions

- What is a "fatty acid"?
- What is the difference between a "fat" and an "oil"?
- What is a "mineral oil"?
- What is the difference between "saturated" and "unsaturated"?
- What does a "cis" arrangement actually mean?
- Why is this arrangement found rather than the "trans" arrangement?
- What is a "conjugated system"?
- What is a "free radical"?
- What is the mechanism of attack on a double bond?
- How is free radical oxygen formed?
- Why do the products of the free radical mechanism smell so unpleasant?
- What is a "peroxide value"?
- What is an "antioxidant"?
- How do antioxidants remove free radicals?
- Ascorbic acid (Vitamin C, E 300) is widely used as an antioxidant e.g in beer and fruit juice. Why is it not used in fats?
- How does time and heat affect oxidation?

These are only some of the questions that could be asked. If you can think of others, please do so.

Possible Investigations

There are many factors here which can be altered and investigated:

1. Fats compared with oils.

2. "Raw" fats and oils compared with commercial equivalents with antioxidants.

3. Oxidation temperature and/ or air flow during the accelerated oxidation of triglycerides.

4. Compare different antioxidants in the above experiment.

5. Synthesis of an antioxidant.

6. Hydrolysis of triglycerides in acidic/alkaline environment.

7. Hydrolysis of triglycerides using enzymes.

8. Examine the effect of Vitamin C and associated compounds on the browning of apples.

These investigations could be linked to the Starter Investigation on Fat and Water in Food.

This list is by no means exhaustive: there are many other possibilities which could be investigated.

Some Sources of Information

Method

"Preparing and Testing an Antioxidant" by P. Wiseman & F. Fitton, *Education in Chemistry* , 1979, **16,** 180.

N.B. An amendment is required in the above paper in the section on antioxidant preparation. In the third line, replace "concentrated hydrochloric acid" with an equivalent concentration of the H^+ from sulphuric acid.

The oxidation of fats can be accelerated by heating them and at the same time bubbling air through them. This could be done, for example, using a water bath at say 60°C. From time to time samples can be tested for their peroxide value. Antioxidants can be added and the experiments repeated to find out how effective they are in preventing air oxidation.

M.Hanssen, *"The New E for Additives:"*, Thomsons, 1987

This lists allowed food additives, including preservatives. Most health food stores will have a number of books with this information.

Help and Hints

Calculating the Peroxide Value
P. Wiseman & F. Fitton, *Education in Chemistry* , 1979, **16,** 180.

To determine the peroxide value of a chosen sample, the following method can be used.

1. Weigh accurately between 5 and 6 g of the chosen sample into a 250 cm^3 stoppered flask. It may be possible to transfer the sample using a 10 cm^3 pipette if the sample is a liquid.

2. Add 30 cm^3 of a 3:2 (by volume) mixture of glacial acetic acid and medicinal paraffin or a less viscous hydrocarbon liquid like hexane.
Swirl the contents of the flask until the sample has dissolved.

3. Add 0.5 cm^3 of saturated potassium iodide solution and allow to stand, with occasional shaking, for one minute. Now add 30 cm^3 of distilled water to the flask.

4. Titrate the contents of the flask with a 0.01 mol l^{-1} solution of sodium thiosulphate until the yellow colour of the iodide has almost disappeared.

5. Add 0.5 cm^3 of starch solution to act as an indicator, and continue the titration until the blue/black colour disappears and record the volume of thiosulphate added.

6. Carry out a second titration using the same reagents but without the sample present to give a blank titration result.

The peroxide value is calculated as follows:

$$\text{Peroxide Value} = \frac{1000\,(s - b)\,c}{\text{mass of sample}}$$

in the above equation
s = titre of sample
b = titre of blank
c = concentration of sodium thiosulphate solution

This gives the peroxide value in milliequivalents per 1000 g of triglyceride.

Testing the Water

Investigation Brief

Many of us take the clean water we get from the kitchen tap for granted and certainly, in Scotland, there seems to be a never ending supply of it! Over 3.5 million litres of drinking water per day is supplied to consumers in Scotland. The average consumer uses about 140 litres of drinking water every day, but over 65% of this is used for baths, showers, washing machines, dishwashers and flushing the toilet. The demand for clean water is greater now than ever before, but how clean is our water?

Many people will be aware of the problems associated with nitrates and phosphates present in fertilisers which have over the years contaminated natural water supplies when they have been washed from the land into rivers and streams. There is no doubt that this process is partly responsible for the increase in the condition known as "**eutrophication**". This condition results in an increase in the amount of algae found in lochs and lakes. The algae grow very quickly when the water becomes "over-nourished" with phosphate and nitrate and the result is the rapid spread of the algae across the surface of the water. This blocks out the sunlight from other plants living in the water, but animals like fish are also affected. The solubility of oxygen in water is quite low and its depletion by the decaying algae that have sunk to the bottom of the loch makes it difficult or impossible for the fish to survive because of the lack of dissolved oxygen. Loch Leven in Fife has been affected by this particular problem in recent years.

The solubility of oxygen decreases with increasing temperature; in addition, algae grow faster in warmer water. These two affects compound the problem for fish in the summer.

Nitrates are a particular problem as they are difficult to remove economically. Excessive amounts are dangerous for babies and are thought to give rise to what is called "blue baby syndrome". In some areas where this is a particular problem such as East Anglia, babies are often given bottled water.

Phosphates can also pose a major problem - its concentration in river water depends not only on the type of farming but also on local industry. A study of the River Kelvin in Glasgow in the 1980's found a dramatic rise in the phosphate concentration at various stages along a stretch of the river. On further investigation one source was traced back to a bus depot which cleaned its buses with a phosphate based detergent. These detergents were then being washed down the drain and entering the natural water system.

Aluminium is widespread in the environment, with several milligrams being swallowed each day in a typical diet. An area of concern has been a possible link between aluminium in water and the medical condition known as Alzheimer's disease, although more recent research seems to have cast some doubt on the link.

The aluminium level in drinking water often increase following the treatment at the water works. This is because aluminium sulphate or aluminium ammonium sulphate ('alum') is added to water to act as a coagulant and remove the peaty brown colouration that much of our water has. Although most of the aluminium is filtered out as a brown insoluble scum ('floc'), some inevitably passes into the drinking water.

Aluminium is not the only metal ion that can be detected in water. Up to 20 different metals are present in trace amounts in our water. Some people may have experienced the effects of levels of manganese and iron in their tap water. As the tap is turned on, the water turns black almost immediately as the metal ions are oxidised. This can be quite unsettling to the householder! Removing these ions can be a very expensive and lengthy process with pH playing a major role in the removal of both ions from the water. The process usually involves conversion of the metal ions to a precipitate by oxidation and then removal of this precipitate by filtration and sedimentation. The pH then has to be readjusted to make the water drinkable.

Some Starter Questions

- Why do nitrates and phosphates in fertilisers pose such a problem?
- What property of these fertilisers make it so easy for them to appear in natural water systems?
- What does "eutrophication" mean?
- What is meant by "dissolved oxygen"?
- Why do algae thrive when the water becomes "over-nourished"?
- How does the solubility of oxygen in water vary with temperature?
- Why are phosphates used in commercial detergents?
- What is meant by the term "coagulant"?
- Why can aluminium sulphate or alum be used as a coagulant?
- What is "Alzheimer's disease"?
- Is aluminium thought to be connected to this condition?
- What other metal ions might be present in water?
- Why do iron and manganese ions oxidise as soon as the tap is turned on?
- Why does the water "turn black"?
- How does pH help to control this process?

These are only some of the questions that could be asked. If you can think of others, please do so.

Possible Investigations

1. How good is our drinking water? Many people these days prefer to drink bottled water and mineral waters believing them to be "better" than ordinary tap water.

   Compare samples of tap water with specialised bottled waters to see which type has the most metal ions, phosphates, nitrates etc. to try and ascertain which is "best"?

2. Relate river or loch phosphate concentrations to species of living organisms in the water.

3. Determination of phosphates and nitrates in river waters at various points on a river from source to mouth and just below tributaries.

   - How do the results relate to land use (e.g. type of farming)?
   - How do the results relate to local industries?
   - How do the results relate to bus cleaning depots?
   - How do the results relate to car wash centres?
   - How do the results relate to sewage treatment plants?

4. How does the amount of dissolved oxygen, nitrates, phosphates and/or metal ions present in fresh water affect the environment and the species living in the natural water system?

   Are there signs of eutrophication present locally? What is causing this?

5. Investigate the process of removing iron and manganese ions from supplies of water by altering the pH of the water.

   - How does pH help to remove these ions from water?
   - What steps have to be taken before water is drinkable?

6. Investigate how to remove the brown colouration of peaty water.

This list is by no means exhaustive: there are many other possibilities which could be undertaken.

Some Sources of Information

Starter Investigation on Phosphates.

"Standard Methods for the Examination of Water and Wastewater, 18th Ed." editors A.E. Greenberg, L.S. Clesceri and A.D. Eaton, American Public Health Association, American Water Works Association and Water Environment Federation, Washington, 1992;

Test Methods for the analysis of water from HMSO in the "Methods for the Examination of Waters and Associated Materials" series.

Scottish Environment Education Council (SEEC),
University of Stirling,
Stirling FK9 4LA.

Scottish Environment Protection Agency (SEPA)
http://www.sepa.org

Water Authorities (Scotland)

East of Scotland Water

North of Scotland Water

West of Scotland Water

Contact information on the above companies can be found in local telephone directories. This will also give local contacts.

Many commercial test kits are available for chlorine, phosphate, aluminium and a selection of other metals.

Test kits are available from:

Camlab Ltd., Nuffield Road, Cambridge CB4 1TH.

Lovibond, The Tintometer Ltd., Waterloo Road, Salisbury SP1 2JY.

Wine Analysis

Investigation Brief

Wine is possibly the most ancient and commonplace of all alcoholic drinks and it forms an integral part of many cultures. Table wine has a particularly complex chemical composition, being a mixture of metal ions and various weak organic acids, as well as alcohols, any of which can affect the quality and taste of the wine. Consequently, careful monitoring and understanding of a wine's chemical composition is of critical importance to the wine industry.

There are four major chemical variables which must be investigated in any efficient wine analysis undertaken by a wine producer : acidity (including non-volatile acids), ethanol content, sulphur dioxide content and tannin content.

The acidity of table wines is caused primarily by various weak organic acids. These carboxylics are essential for taste and also for their preservative qualities. Generally, a wine's acidity is gauged in terms of the total acidity, being a measure of the $[H^+]aq$ concentration in solution. Some of the acids can escape as vapour: these are referred to as volatile acids.

Secondly, the alcohol (ethanol) content of the wine is of great importance. The fermentation process, which produces the alcohol, is governed by yeast cells (which occur naturally on the skins of grapes) acting on the sugars present in the grapes. While wild yeast occur naturally on the skin of grapes (as a white 'bloom') they are killed by sulphite in most commercial wine making: specially bred yeast cultivars are then used. (These can be obtained from 'Home Brew' shops). Fermentation stops when the ethanol content reaches about 15% by volume. The reason for this is complex.

Thirdly, sulphur dioxide is an essential chemical additive to wine, both for its antioxidant (reducing) properties and for its role as a bactericide. It is usually added as sodium metabisulphite, commonly called 'sulphite'. A wine with too little added sulphur dioxide will be subject to bacterial oxidation, giving rise to the sour taste of ethanoic acid (vinegar).

$$CH_3CH_2OH \longrightarrow CH_3COOH$$

Most of the added sulphur dioxide combines with aldehydes and ketones present in the wine, with the residual SO_2 protecting the wine from bacterial attack. However, an excess of sulphur dioxide will be obvious to the palate and its unpleasant smell and dry taste will spoil the wine's bouquet. There are legal limits governing its level in most countries.

Finally, the tannin content of a wine is of fundamental importance. Tannins are large polyphenol compounds which give the 'bite' to red wine: too little tannin and the wine tastes dull and flat, however, too much tannin and the wine will taste bitter and soured. These derive from the skins of red grapes or can be extracted from oak (barrels or added as chips).

Some Starter Questions

- What is meant by "volatile" and "non-volatile acids"?
- How could the acidity of a chosen wine be measured?
- How is the concentration of an acid normally measured?
- Are there any special factors in measuring acid concentration which might have to be considered?
- How might small quantities of non-volatile acids be detected?
- Why are non-volatile acids so important in wine making?
- What technique could be used to separate the volatile acids present in a sample of wine?
- How could the ethanol content of a wine be measured?
- How is the ethanol content measured in the brewing industry?
- How is the ethanol content measured in home brews?
- Could these methods be applied here?
- What part does sulphur dioxide play in wines?
- What kind of reaction does sulphur dioxide undergo?
- Is there any connection between your course work and a technique for measuring sulphur dioxide content?
- What is a "tannin"?
- How could the amount of tannins present in certain wines be measured?

These are only some of the questions that could be asked. If you can think of others, please do so.

Possible Investigations

1. Comparison of chemical composition of wines of a region/nation etc.

2. Comparison of white and red wines.

3. Comparison of 'home-made' and 'shop-bought' wines.

4. Comparison of wine made with brewer's yeast and wine made with baker's yeast.

5. Investigation of how chemical components vary during the fermentation process.

6. Comparison of grape varieties.

7. Comparisons with ciders and beers.

8. Why are white wines served chilled and red wines served at room temperature? Does this have something to do with volatile acids?

This list is by no means exhaustive: there are many other possibilities which could be investigated.

Some Sources of Information

"Analysis of Wine - An Undergraduate Project" by P.R. Haddad , M. Sterns and J. Wardlaw , *Education in Chemistry,* 1978, **15**, 87.

"Sulphur Dioxide and Tannin" G.W.A. Fowles , *Education in Chemistry,* 1978, **15**, 89.

Selinger B. K. , "*Chemistry In The Marketplace. 4th Ed.*", London, 1991.

Help and Hints

A. *ACIDITY*

1a. ***Acidity*** : 100 cm^3 of the chosen wine should be collected and its pH measured. Next, a pH titration should be carried out using 0.1 mol l^{-1} NaOH. The titration curve of pH versus volume of NaOH added should be plotted and used to determine the volume of NaOH required to reach pH 8.3 (Why is the equivalence point used greater than 7?) The titration procedure should be repeated to achieve duplicate results. This gives a measure of the total acidity in terms of number of moles of NaOH required per 100 cm^3 of wine.

In order to determine the non-volatile acidity and thus the volatile acidity, two 25 cm^3 samples of wine are evaporated down to approximately 5 cm^3. Next, approximately 25 cm^3 of distilled water is added to each, and the process repeated. The final solutions are diluted to 30cm^3 and the titration procedure repeated. This yields the fixed acidity of the wine; subtraction then gives the volatile acidity.

Note: Although the acidity of a wine is important, it is the pH of the wine that plays the more important role in terms of taste. The pH of a wine relates to the colour as well as taste : a low pH gives a desirable translucent colour due the ionisation of anthocyanins which are wine colourants.

A wine's pH also controls the sulphur dioxide preservative action. Typically, sulphur dioxide exists as bisulphite complexes within the wine; however, when the wine's pH is low the concentration of $SO_{2(aq)}$, which is an antimicrobial agent, increases.

$$2H^+_{(aq)} + SO_3^{2-}{}_{(aq)} \longrightarrow H_2O_{(l)} + SO_{2(aq)}$$

1b. ***Detection of non-volatile acids by thin-layer chromatography*** : It is possible to detect the presence of relatively non-volatile acids in wine using thin-layer chromatography (TLC). TLC is of particular importance in the wine industry as it is used to monitor the enzyme catalysed conversion of the stronger malic acid to the weaker lactic acid. This allows the acidity of fermenting wine to be monitored.

To carry out a TLC analysis, take a 10 cm^3 sample of wine and evaporate it to 1 cm^3 on a water bath. (Red wine must first be decolourised with activated charcoal to remove any pigments and then filtered). The concentrated solution is applied to a TLC plate along with standard solutions of lactic, malic, succinic and tartaric acids.
The plate is developed in an eluent mixture (n-butanol : formic acid : water in the ratio 8 : 1 : 2·5).

Finally, the plate is dried overnight to remove all traces of formic acid, and sprayed with the acid/base indicator bromocreosol green to visualise the acid and allow Rf values to be calculated.

B. *ETHANOL CONTENT*

There are two methods which are widely used to determine the ethanol content of a wine.

1. ***The density method.*** A 50 cm^3 sample of wine is made slightly alkaline with NaOH and then distilled until half of it has distilled over. The distillate is transferred to a 50 cm^3 flask and topped up with water. Its density is measured. (Keep this solution for the second part of the experiment) Prepare a series of ethanol solutions of known composition, measure their densities , and plot a graph of density versus composition. From this graph the composition of the sample can be identified.

2. ***The oxidation method***: The ethanol content is determined by dichromate oxidation.

$$2K_2Cr_2O_7 + 3CH_3CH_2OH + 8H_2SO_4 \longrightarrow 3CH_3COOH + 2K_2SO_4 + 2Cr_2(SO_4)_3 + 11H_2O$$

An excess of dichromate is used, and a back titration is used to determine the amount of excess dichromate. A standard (0.1 mol l^{-1}) solution of Iron (II) ammonium sulphate, $Fe(NH_4)_2(SO_4)_2.\ 6H_2O$, is used. The equation for this reaction, in its ionic form, is

$$Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$$

The titration is carried out by pipetting two 25 cm^3 samples of 0.1 mol l^{-1} potassium dichromate into two conical flasks. Then exactly 1 cm^3 of ethanol solution, from the previous experiment, is added and heated in a water bath to allow oxidation to occur.

The mixture is transferred into two titration flasks and 150 cm^3 of distilled water added along with 10 drops of indicator (N-phenylanthranilic acid). This dark brown mixture is titrated with a solution of iron (II) ammonium sulphate, which has been standardised against the potassium dichromate solution, until the first appearance of a dark green colour.

C. *SULPHUR DIOXIDE CONTENT*

The sulphur dioxide content is determined via the redox reaction

$$SO_2(aq) + I_2(aq) + 2H_2O(l) \longrightarrow 4H^+(aq) + SO_4^{2-}(aq) + 2I^-(aq)$$

To obtain the free SO_2 content the wine is first acidified with 25% H_2SO_4, and then titrated with 0.01 mol l^{-1} I_2 using starch as the indicator.

The total SO_2 content is obtained by first making the wine alkaline with 0.1 mol l^{-1} NaOH, to break down the bisulphite complexes, and then it is acidified and titrated.

D. *TANNIN CONTENT*

To determine the tannin content of a wine 5 cm^3 of the wine is diluted to 15 cm^3 with distilled water and heated gently on a hotplate until the volume has been reduced by about half. *Remember that the vapours are flammable - no naked flames.* This removes the alcohol. The resultant solution is made up to 250 cm^3 with distilled water and titrated with 0.004 mol l^{-1} $KMnO_4$ using indigo carmine as the indicator. This is titre X.

Next 1 g of activated charcoal is added to 25 cm^3 of wine to decolourise it. This removes tannins. 5 cm^3 of the decolourised wine is filtered and pipetted into a flask and the above procedure repeated. This is known as a blank titration and allows the oxidation of the indicator and any other oxidisable compounds, other than the tannins, to be taken into account. This is titre Y.

The amount of $KMnO_4$ needed to oxidise the tannins is X - Y = Z.

As composition of tannins is variable, the titration is referred to a hypothetical purified tannin for which 1 cm^3 of 0.004 mol l^{-1} $KMnO_4$= 0.832 mg of tannin.

$$\text{Hence, percentage tannin in wine} = \frac{0.832 \times Z \text{ mg}}{5000 \text{ mg}} \times 100$$

$$= 0.01664Z$$

This calculation assumes that 1 cm^3 of wine weighs 1 g