ACTIVITY BRIEF

Preparing and testing a synthetic dye

The science at work

Synthetic dyes have replaced natural dyes almost completely for dyeing fabrics and textiles. An understanding of why some compounds have intense colours and how these compounds can interact with natural and synthetic fibres enables scientists to design and make dyes.

Your brief

You need to prepare a synthetic dye, investigate its effectiveness to dye three different fabrics and write a detailed report of your work.

Task 1 About synthetic dyes

Complete Study sheet: Synthetic dyes. Keep your answers in your portfolio.
This will give you a good background to the chemistry of synthetic dyes.

Task 2 Preparing and testing a synthetic dye

Obtain a copy of Practical sheet: Azo dyes. Read about the chemistry of azo dye formation. Then carry out the small scale preparation of the azo dye formed from phenylamine and 2-naphthol. This will give you experience of techniques used to make azo dyes.

Now follow the instructions to prepare an azo dye and test its effectiveness on different textiles.

You are given the chemical structures of twelve azo dyes. You need to choose one of them to make and test. Most of the information you need is on the sheet though you may wish to do some further research.

For your chosen dye:

- write its structural formula and label the functional groups responsible for its colour
- identify the starting materials you need
- outline the method you will use and list the chemicals and apparatus needed
- make a risk assessment.

Check the method with your teacher. After making any necessary modifications, carry out some trials using the suggested extraction method. In your portfolio, make a note of any changes to the method, with your reasons, and write out in full the method to be used.

Select three fabrics to dye.

In your portfolio:

- write the names of the chosen fabrics, together with the structural formulae of the molecules that make up the fabric
- suggest how the dyes might be attached to the fabrics.

Note: You may be able to use multi-fibre strip. Ask your teacher.

In another activity you will look at scaling up production to an industrial scale.

**Task 3 Writing your report**

Write a report of your work. This should describe the purpose of the work, the key findings and your conclusions. Key data may be taken from your portfolio and presented in a form that makes it easier for the reader to understand.

You do not need to write out all your work again. You may cross-reference information you found (together with their source) and data recorded during your practical work in your portfolio, during the investigation.
STUDY SHEET

Synthetic dyes

You do not need to remember all the information on this sheet.
However, working through the questions will give you a good background for the practical work to come.

Commercial dyes are classified according to how they are used and for what they are used. They are listed by The Society of Dyers and Colourists in its Colour Index. The dyes are assigned a C.I. number.
At the end of this study sheet you’ll find examples of synthetic dyes. Use them to answer the questions below.

Note: It may help you to picture these molecules if you make molecular models of them. It will take a little while to make them, so work with others to share the workload.

Acid dyes

Acid dyes are used mainly for wool and polyamides. They are anionic and applied in an acid dye bath.

Questions
1. Identify acid dye molecules in the examples given. On the drawings, indicate and name the chromophores.
2. Explain how the dyes become anionic when they dissolve in water.
3. Explain why some dyes contain –SO₃Na groups rather than –SO₃H groups.

Basic dyes

Basic dyes may be used to dye cotton, but they do not show good fastness properties. They are cationic dyes (in other words, the opposite of acid dyes).

Questions
4. Identify the basic dye amongst the examples given. On the drawing of its structure, indicate and name the chromophore.
5. On the drawing, indicate the cationic group.
6. Draw a sketch to show the bonding in an ammonium ion. Use it to explain the bonding in the cationic part of the dye.

Disperse dyes

Disperse dyes are almost insoluble in water. They are milled to an extremely small particle size. They are used to dye ethanoylated cellulose fibres and polyesters.
Questions
7 Identify the disperse dyes in the examples given. On the drawings, indicate and name the chromophores.
8 Explain why these are insoluble while acid dyes and basics dyes are soluble in water.

Direct dyes
These are anionic dyes that may be used with cotton and reformed cellulose fibres. They are soluble in water.

Questions
9 Identify the direct dyes in the examples given. On the drawings, indicate and name the chromophores.
10 Explain why these direct dyes are soluble in water, labelling the drawings to support your explanation.

Reactive dyes
Reactive dyes are coloured compounds that can form covalent bonds with the fibre molecules in a textile. Different ones have been synthesised to dye both some natural and some synthetic fibres.

For example, dyes have been made that have this group:

![Dye structures](image)

Hydroxyls group in cellulose react with the C-Cl group in the dye to form a covalent bond between dye and cellulose molecules.

Questions
11 Identify the reactive dye in the examples given. On the drawing of its structure, indicate and name the chromophore.
12 Explain why the dye you identified in question 11 is soluble in water, labelling the drawing to support your explanation.
13 Find the structure of a cellulose molecule. Draw one of the glucose units in the chain. Describe the reactions that could take place between the dye you identified in question 11 and glucose units in cellulose (use diagrams to illustrate your answer).

Vat dyes
Vat dyes are insoluble in water. However, they can be reduced to a water-soluble form (the leuco form). Once a textile has been soaked in a solution of the reduce form, it is washed in a solution of an oxidising agent. This oxidises the leuco form to the coloured reduced form.
An important example is indigo (the dye used in blue jeans):

![Indigo structures](image)

**Question**

14 Look at the structures of the reduced and oxidised forms of indigo.
   a. highlight the parts of the two structure that differ
   b. indicate the chromophore.
Examples of synthetic dyes

C.I. Acid Blue 6, 17185

C.I. Acid Blue 47, 62085

C.I. Acid Red 25, 16050

Scarlet cationic dye (BP 957364, Ciba)

C.I. Acid Blue 6, 17185

C.I. Disperse Black 2, 112255

C.I. Disperse Red 15, 60710

C.I. Disperse Black 2, 112255
C.I. Direct Red 28, 22120 (Congo Red)

C.I. Direct Green 28, 141155 (Chlorantine Fast Green 5GILL)

Cibacron Brilliant Red B (CGY)
Chemistry of azo dye formation

Stage 1: Diazotization

An aromatic amine reacts with nitrous acid to give a diazonium salt. For example: phenylamine reacts with dilute hydrochloric acid to form phenylammonium chloride. This forms a diazonium salt when reacted with nitrous acid.

\[
\begin{align*}
\text{NH}_3^+ & \quad \text{NaNO}_2 \\
& \quad \text{HCl, H}_2\text{O} \\
& \quad 0 - 5 \degree \text{C}
\end{align*}
\]

Stage 2: Coupling

The diazonium salt reacts with a coupling compound, usually a phenol. For example: the diazonium salt of phenylamine reacting with 2-naphthol.

Small scale preparation of an azo dye

The purpose of this preparation is to give you experience of techniques used to make azo dyes.

Use the procedure below to make a sample of the azo dye formed from phenylamine and 2-naphthol.

Health and safety

Consult a risk assessment for this procedure and consider whether it needs to be adapted to suit the particular conditions under which you are working. Implement the control measures identified, modifying them as necessary, but first ask your teacher to check your risk assessment. Wear goggles.
Equipment and materials

- 1 x 250 cm³ and 1 x 400 cm³ beakers
- test tube
- goggles
- dropping pipette
- 25 cm³ measuring cylinder
- 2 stirring rods
- thermometer
- phenylammonium chloride (C₆H₅NH₃Cl) [TOXIC; rapidly absorbed through the skin so wear nitrile gloves]
- 2 mol dm⁻³ hydrochloric acid [IRRITANT]
- 10% w/w solution of sodium nitrite [HARMFUL]
- 2-naphthol [HARMFUL]
- 2 mol dm⁻³ sodium hydroxide solution [CORROSIVE]
- crushed ice
- filtration apparatus (preferably reduced pressure)
- melting point apparatus (if melting point is to be determined)
- oven at 105 °C

Procedure Read the whole procedure before starting.

1 Prepare these two solutions:

   Solution A. Tare a 250 cm³ beaker. Add 1 g phenylammonium chloride and then 5 cm³ distilled water. Add 10 cm³ of 2 mol dm⁻³ hydrochloric acid, stir well and put the beaker in ice-bath to cool to about 5 °C.

   Solution B. Measure 18 cm³ of 2 mol dm⁻³ sodium hydroxide solution into another 400 cm³ beaker. Add 2 g of 2-naphthol. Stir to dissolve and dilute to 100 cm³.

2 Add 10 cm³ of 10% w/v sodium nitrite solution drop by drop to solution A, stirring continuously. Make sure the temperature keeps below 10 °C. If it rises rapidly add a small piece of ice. When the addition is complete, leave the mixture to stand in an ice bath for 5 minutes (yellow crystals may begin to form).

   Check the reaction is complete by taking 1 drop of the reaction mixture and adding it to 1 cm³ acidified potassium iodide solution. If the potassium iodide solution turns deep purple, add more sodium nitrite solution to the reaction mixture.

3 Pour the mixture slowly, with stirring, into solution B. Leave to stand while the precipitate settles to the bottom of the beaker. Filter the solid, preferably under reduced pressure, wash well with water. Remove the filter paper and precipitate, lay it on a watch glass and put in an oven at about 105 °C.

4 Tare a sample tube and scrape the dried product into it. Weigh and calculate the yield of azo dye.

5 Calculate a) the theoretical yield of azo dye based on the mass of phenylammonium chloride you used, and (b) the percentage yield.
Prepare an azo dye and test its effectiveness on different textiles

Look at the structures of azo dyes below. If you are able, work in a group with each member making a different dye so that you can compare your results.
Once you have studied the structures of the azo dyes:
- select one to make
- list the starting materials required.

Now look at the methods summarised below. Use them to plan the preparation of the dye you have chosen and a method for testing its effectiveness.

**From aminobenzenesulfonic acids**

*Stage 1: Diazotisation*

Wear goggles.

Measure $2.8 \times 10^{-3}$ moles of the aminobenzenesulfonic acid [IRRITANT] into a test tube. Add 5 cm$^3$ of 2.5 mol dm$^{-3}$ sodium carbonate solution and warm in a water bath until the solid dissolves. Remove the test tube from the water bath and add 0.2 g sodium nitrite [TOXIC] [OXIDISING] dissolved in 0.5 cm$^3$ distilled water.

Weigh about 3 g of crushed ice into a second test tube. Add 0.53 cm$^3$ of concentrated hydrochloric acid [CORROSIVE]. Now add dropwise the solution from the first test tube. Stand the test tube containing the mixture in a beaker of crushed ice.

*Stage 2: Coupling*

Measure $2.6 \times 10^{-3}$ moles of the coupling compound [HARMFUL] into a 25 cm$^3$ conical flask. Add 2 cm$^3$ of 2.5 mol dm$^{-3}$ sodium hydroxide solution [CORROSIVE] and stand the flask in crushed ice.

Add the mixture from stage 1 a little at a time, stirring with a glass rod after each addition. Continue stirring the reaction mixture for a further 10 minutes. Heat the mixture in a hot water bath until any solid material present dissolves. Add 1 g sodium chloride and continue the heating until it has dissolved.

Cool the reaction mixture to room temperature. Then stand the flask in crushed ice. Filter the precipitate under reduced pressure. Wash the solid with 2 cm$^3$ saturated sodium chloride solution and leave the product to dry in the air. Weigh your product.

*Dyeing a multi-fibre strip*

Wear disposable gloves.

Dissolve 0.5 g of the azo dye in 20 cm$^3$ of distilled water. Put a piece of the multi-fibre strip in the solution. Boil the solution for 5 minutes making sure the strip is immersed throughout. Use tweezers to remove the strip and rinse it with tap water. Pat the dyed fibre dry with a paper towel and leave to dry.

**From 4-nitrophenylamine**

*Stage 1: Diazotisation*

Wear goggles.

Measure 1.5 cm$^3$ of distilled water into a small test tube and add 1.5 cm$^3$ concentrated hydrochloric acid [CORROSIVE]. Stand the test tube in crushed ice.

Into another test tube, measure 0.005 moles of 4-nitrophenylamine [TOXIC], 0.0055 moles of sodium nitrite [TOXIC] [OXIDISING] and 1.5 cm$^3$ of distilled water. Mix well and stand the test tube in crushed ice. Add this mixture dropwise to the hydrochloric acid while stirring.
with a glass rod. Continue stirring occasionally for a further 10 minutes. Filter to remove any solid material and keep the filtrate in a clean test tube.

**Stage 2: Coupling**

Measure 0.0051 moles of the coupling compound [HARMFUL] into a 25 cm$^3$ conical flask. Add 10 cm$^3$ of 2.5 mol dm$^{-3}$ sodium hydroxide solution [CORROSIVE] and stand the flask in crushed ice.

Add the filtrate from stage 1 dropwise with stirring and leave the flask to stand in crushed ice for 10 minutes. Now add about 1.5 cm$^3$ of concentrated hydrochloric acid to the mixture until the pH is 3-4. Add 1 g sodium chloride and heat the conical flask until the mixture is just boiling. Cool the mixture to room temperature and then in crushed ice. Filter under reduced pressure and wash the solid with 2-5 cm$^3$ of distilled water. Leave it dry.

Weigh your product.

Note: If no solid forms, the solution can be used to dye the fabrics directly.

**Dyeing a multi-fibre strip**

Wear disposable gloves (preferably nitrile gloves).

Dissolve 0.5 g of the azo dye in 20 cm$^3$ of distilled water. Add 3 cm$^3$ of a 2.5 mol dm$^{-3}$ sodium hydroxide solution and heat the mixture in a hot water bath. Stir the mixture with a glass rod.

Put a piece of the multi-fibre strip in the solution. Boil the solution for 3 minutes making sure the strip is immersed throughout. Use tweezers to remove the strip and rinse it with tap water. Pat the dyed fibre dry with a paper towel and leave to dry.

When you have studied the methods:

- choose an appropriate summary method
- write a procedure, together with an equipment and materials list, and make a risk assessment
- prepare a sample of the dye
- test the effectiveness of the dye on different textiles. Note: a convenient way to do this is by using multi-fibre strip.
Teacher notes

This activity links to AQA A2 Unit 13 Colour chemistry.

One assessment requirement for the unit is that students must produce:

- a report detailing the preparation of a synthetic dye together with details of its application to three different fabrics including:
  - identifying your chosen dye and researching a method for its preparation
  - detailing the type of dye and the method used to make it, the scientific principles underlying the process together with the apparatus used and any appropriate risk assessments

with the highest marks gained if they show that (this has been taken from the specifications)

- Thorough research has produced comprehensive and workable method of preparing a synthetic dye that is firmly rooted in science.
- Initial plan into a method of preparing a synthetic dye was comprehensive with no error and yielded workable methods. Appropriate modifications to the method of preparation of the dye are suggested.

No advice is given on how students might ‘identify’ their ‘chosen dye’. The approach taken here is to give a list of azo dyes and ask students to select one of them. They then need to work out what chemicals are needed to make the dye. Then they look at the outline procedures, select a suitable one and develop it into a detailed method.

The awarding body places some emphasis on the research aspect, but this is likely to lead to a specific method for a specific dye – and it’s not easy to see what the planning process might involve. Hence the approach taken in this activity in the Practical sheet: Azo dyes.

A different azo dye can be made using ethyl 4-aminobenzenecarboxylate [IRRITANT]. This is a safer alternative to phenylamine/ phenylammonium chloride [TOXIC]. See CLEAPSS guide L195. 6.1. You might want to consider this alternative if you are unhappy using phenylamine with your group of students. However, you will need to alter the practical sheet (diagrams and method).

Synthetic dyes

Acid dyes

1 Identify acid dye molecules in the examples given. On the drawings, indicate and name the chromophores.

Answer:
C.I. Acid Red 25 the azo group
C.I. Acid Blue 6 the azo group
C.I. Acid Blue 47 the anthroquinone group
2 Explain how the dyes become anionic when they dissolve in water.
   \[ -\text{SO}_3\text{H} + \text{H}_2\text{O} \rightarrow -\text{SO}_3^- + \text{H}_3\text{O}^+ \] (benzenesulfonic acids are strong acids)
   \[-\text{SO}_3\text{Na} + \text{aq} \rightarrow -\text{SO}_3^-\text{(aq)} + \text{Na}^+(\text{aq}) \]

3 Explain why some dyes contain \(-\text{SO}_3\text{Na}\) groups rather than \(-\text{SO}_3\text{H}\) groups.
   \[-\text{SO}_3\text{H} + \text{NaOH} \rightarrow -\text{SO}_3\text{Na}^- + \text{H}_2\text{O} \]

**Basic dyes**

Basic dyes may be used to dye cotton, but they do not show good fastness properties. They are **cationic** dyes (in other words, the opposite of acid dyes).

4 Identify the basic dye amongst the examples given. On the drawing of its structure, indicate and name the chromophore.
   \[ \text{Scarlet cationic dye (BP 957364, Ciba)} \text{ the azo group} \]

5 On the drawing, indicate the cationic group.
   \[ \text{The group surrounding N}^+ \]

6 Draw a sketch to show the bonding in an ammonium ion. Use it to explain the bonding in the cationic part of the dye.
   \[ \text{Students should see the similarity between the quaternary ammonium ion in the dye and NH}_4^+. \text{ They should describe the bonding as three single covalent bonds and one dative covalent bond.} \]

**Disperse dyes**

Disperse dyes are almost insoluble in water. They are milled to an extremely small particle size. They are used to dye ethanoylated cellulose fibres and polyesters.

7 Identify the disperse dyes in the examples given. On the drawings, indicate and name the chromophores.
   \[ \text{C.I. Disperse Black 2 the azo group} \]
   \[ \text{C.I. Disperse Red 15 the anthroquinone group} \]

8 Explain why these are insoluble while acid dyes and basic dyes are soluble in water.
   \[ \text{They have no strongly ionisable groups in their structure.} \]

**Direct dyes**

These are anionic dyes that may be used with cotton and reformed cellulose fibres. They are soluble in water.

9 Identify the direct dyes in the examples given. On the drawings, indicate and name the chromophores.
   \[ \text{C.I. Direct Red 28 the two azo groups} \]
   \[ \text{C.I. Direct Green 28 the azo group} \]

10 Explain why these direct dyes are soluble in water, labelling the drawings to support your explanation.
   \[ \text{C.I. Direct Red 28 there are two \(-\text{SO}_3\text{Na}\) groups} \]
   \[ \text{C.I. Direct Green 28 there are one \(-\text{SO}_3\text{Na}\) group and one \(-\text{COO}\text{Na}\) group} \]
Reactive dyes

11 Identify the reactive dye in the examples given. On the drawing of its structure, indicate and name the chromophore.  
   Answer: Cibacron Brilliant Red B (CGY) the azo group

12 Explain why the dye you identified in question 11 is soluble in water, labelling the drawing to support your explanation.  
   Answer: there are three –SO₃H groups which ionise in water

13 Find the structure of a cellulose molecule. Draw one of the glucose units in the chain. Describe the reactions that could take place between the dye you identified in question 11 and glucose units in cellulose (use diagrams to illustrate your answer).  
   Answer: Students need to identify a condensation reaction that can take place, eliminating a water molecule.

Vat dyes

14 Look at the structures of the reduced and oxidised forms of indigo.
   a highlight the parts of the two structure that differs  
      Answer: marked by the ovals on the diagrams below
   b indicate the chromophore  
      Answer: within the oval below on the indigo structure (structure on the left)

Azo dyes

Small scale preparation of an azo dye

The purpose of this preparation is to give students experience of techniques used to make azo dyes. The control of temperature is vital and this practical gives them an opportunity to practice.

Each student or pair of students will need:
- 1 x 250 cm³ and 1 x 400 cm³ beakers
- test tube
- dropping pipette
- 25 cm³ measuring cylinder
- 2 stirring rods
- thermometer
- phenylammonium chloride [TOXIC; rapidly absorbed through the skin so wear nitrile gloves]
- 2 mol dm\(^{-3}\) hydrochloric acid [IRRITANT]
- 10% w/w solution of sodium nitrite [HARMFUL]
- 2 mol dm\(^{-3}\) sodium hydroxide solution [CORROSIVE]
- crushed ice
- filtration apparatus (preferably reduced pressure)
- melting point apparatus (if melting point is to be determined)
- oven at 105 °C

**Note:** If time allows, students might be asked to recrystallise a small sample from glacial ethanoic acid [CORROSIVE] and, after drying, measure its melting point. The melting point of the pure dye is 131 °C.

### Prepare an azo dye and test its effectiveness on different textiles

This part works well if students work as a class, with each member selecting a different azo dye to make. The ones given provide a range of colours.

Having selected a dye, students need to work out what starting materials are needed. Check they get this right.

Then they choose the appropriate summary method. They need to write a detailed procedure, including the quantities of chemicals to be measured out and listing equipment and materials needed. They must make a risk assessment which must, of course, be checked by a competent person before the practical work is started.

For the dyeing, students might investigate different dyeing conditions (based on the outline methods provided), for example, temperature, time and dye concentration. They should look at the depth of colour and its fastness to washing.

It is suggested that they use multi-fibre strip (see below). It is relatively inexpensive and will reduce the number of experiments to set up to investigate dyeing effectiveness.

Each student or pair of students will need:

- depending on the azo dye: 2-aminobenzenesulfonic acid, 3-aminobenzenesulfonic acid, 4-aminobenzenesulfonic acid [all CORROSIVE or IRRITANT] or 4-nitrophenylamine [TOXIC]
- depending on the azo dye: 1-naphthol, 2-naphthol or 2-hydroxybenzoic acid [all HARMFUL and IRRITANT]
- sodium nitrite [solid is TOXIC]
- concentrated hydrochloric acid [CORROSIVE]
- 2.5 mol dm\(^{-3}\) sodium hydroxide [CORROSIVE]

All the chemicals are available from Aldrich Chemicals.

- **SDC Multifibre Strip**
  
  The SDC Colour Experience (Museum) handles the supply to educational establishments at a greatly reduced rate. The price is £2/metre plus VAT plus a charge of £1/order to cover postage and packing.
The SDC multifibre test fabric is made up of 6 different fibres: each is a band of about 15 mm. The fibres are: secondary cellulose acetate (Dicel); bleached unmercerized cotton; nylon 6.6; polyester (Terylene); acrylic (Courtelle); wool worsted.

SDC Colour Experience, Perkin House, 1 Providence Street, Bradford, BD1 2PW
telephone 01274 390955; fax 01274 392888; www.colour-experience.org