# Student's document

## DYEING FOR COLOUR: Making and testing azo dyes

Synthetic dyes have almost completely replaced natural ones for dyeing fabrics and textiles. Promising compounds with the right colour, suitability for the intended fabric and fastness to light and washing are made in gram quantities in the laboratory. This is the start of the process to find out how good yields may be obtained quickly, efficiently and effectively.

But it's one thing to successfully make a compound in the laboratory. Scaling up to industrial scale to make 500 kg, can pose problems. It's quick and easy to weigh one gram of starting material, transfer it to flask and add other chemicals. Imagine doing this with kilograms of starting material. How would you measure them out and transfer them quickly? What would you use for a reaction vessel? And we haven't even mentioned heating up or cooling down reaction mixtures.

### Your brief

Azo dyes are an important group of synthetic dyes. Your brief is to make a range of azo dyes in the laboratory and investigate the importance of temperature control. You need to think about problems that might be encountered when the dyes are made on an industrial scale. You need to produce a wall chart, aimed at 14-19 year old chemistry students, that shows the steps in the preparation and how these are carried out in a pilot plant or a manufacturing plant.

### Your investigation

The investigation is made up of several tasks. Work in a small group to share the workload and make sure you work within the time limit set by your teacher. Careful planning is essential. Your teacher will organise the groups.

Each member of the group should have copies of these **sheets**: *Investigating Sudan I*; *Temperature control on a large scale*; *Preparation of azo dyes*.
One copy of each of *Scaling up* and *Chemical plant* will be given to your group.

*Planning*

This is a lot of work. It's very unlikely that one person could complete it all in the time available. But a thoughtfully organised team could. These are the tasks to be completed:

<u>Individually or in pairs</u>

- investigate the preparation of the azo dye Sudan I (using **sheet** *Investigating Sudan I*)
- investigate the problem of heating or cooling reaction mixtures on a large scale (**sheet** *Temperature control on a large scale*)
- prepare a number of azo dyes (**sheet** *Preparation of azo dyes*)

- each person in your group should make one dye, so the number the group can make depends on how many are in your group
- write equations for the reactions that take place (your teacher will help you)
- use a digital camera to take photographs that illustrate important steps in the syntheses.

This practical work may be shared amongst the group. However, each member should make one azo dye.

A risk assessment must have been done before any practical work is carried out.

Whole group, using *Scaling up* and *Chemical plant*:

- find out how steps in a laboratory synthesis are done at pilot or industrial scale

You will find this website really helpful:
http://www.atworkwithscience.com/Page/ViewTask.aspx?TaskID=7&ModuleID=1
Although it is about scaling up the preparation of a pharmaceutical product, the principles apply to all scale-ups.

- make a wall chart to show the key stages in making a typical azo dye.

**Your findings**

Keep notes describing the practical work you did and key points from discussions you had with others in your group. The wall chart should be put on display so that your teacher and others may see it. You may, as a group or individually, be asked questions about the wall chart.

**Student self assessment**

In 50-100 words describe:

- what scientific skills and knowledge you used and how effectively you used them
- how you worked as a team, giving examples of how you supported others in your group or were supported by them
- how you managed your time and workload
- techniques you used to write and illustrate the article.

# Student sheet: Investigating Sudan I

## Preparation and testing of Sudan I

Sudan I is a red azo dye made from phenylamine and 2-naphthol. Prepare a solution of the dye on a microscale and use it to dye cotton.

*Equipment and materials*

- 2 x boiling tubes
- test tube and rack
- 400 $cm^3$ beaker
- spatula
- tweezers
- dropping pipette
- distilled water
- 5 $cm^3$ measuring cylinders
- balance
- cotton square
- glass rod
- phenylamine
- 2-naphthol
- concentrated  hydrochloric acid
- 15 g/100 $cm^3$ solution of sodium nitrite
- 2 mol $dm^{-3}$ sodium hydroxide
- crushed ice
- nitrile gloves

*Procedure*

1. Put 8 drops of phenylamine in a boiling tube and add 30 drops of distilled water followed by 15 drops of concentrated hydrochloric acid. Shake the boiling tube to mix the contents and then put it in an ice bath.
Measure 1 $cm^3$ of a 15 g/100 $cm^3$ sodium nitrite solution in a second test tube. Cool in the ice bath and pour into solution of phenylamine in hydrochloric acid. Shake to mix well and keep in the ice bath. This is solution **A**.

2. Weigh 0.45 g of 2-naphthol into another boiling tube. Add 3 $cm^3$ of 2 mol $dm^{-3}$ sodium hydroxide solution. Swirl to dissolve. This is solution **B**.

3. Take a piece of cotton cloth 1 cm x 1 cm and, using tweezers, dip it into solution **B**. Make sure the solution completely soaks the cotton. Then dip the cotton into solution **A**. Make sure it is completely immersed. Leave for a minute or two and take the dyed cloth out, wash it under the tap and leave to dry. Note the colour.

## The importance of temperature control

The following experiment shows you one example of what can happen if the temperature of a reaction mixture is not controlled.

*Additional equipment*

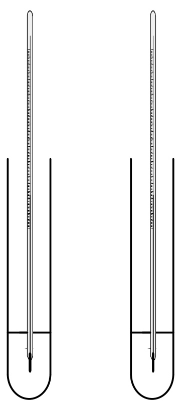
- 2 x thermometers (-10 to 110 $^{o}C$) - ideally rapid response
- boiling tube
- 5 $cm^3$ measuring cylinder
- stopwatch

*Procedure*
Repeat the procedure, but with this change after step 1.

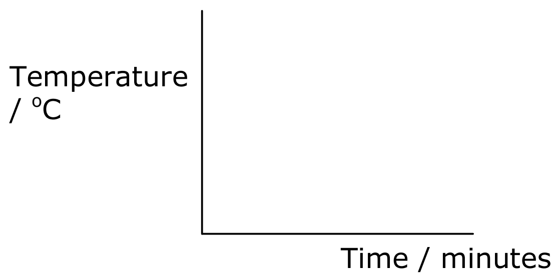
Pour 5 $cm^3$ of water into a clean boiling tube and place it in the same ice bath as solution **A**. Put a thermometer into each boiling tube. Note: Ideally, low heat capacity (rapid response) thermometers should be used, e.g. digital thermometers with Pt-resistance or thermocouple or thermistor sensors. Your teacher will advise you.

When both solutions have reached the temperature of the ice bath, take the ice bath away. Record (a) the temperature of each mixture every 30 seconds until it is constant, (b) record your observations.

Plot graphs of temperature against time.



solution **A**     distilled water




Now carry out steps 2 and 3 with this room temperature solution **A** and compare your observations with those when solution **A** was ice-cold.

Use textbooks and/or an Internet search to help find an explanation for what happened.

## Student sheet: Temperature control on a large scale

From your investigation of Sudan I you will have found temperature control is essential when making an azo dye. In the laboratory, temperature control is often quite straightforward. But what are the problems if several tonnes (1 tonne = 1000 kg) of reaction mixture are being used?

### Prediction

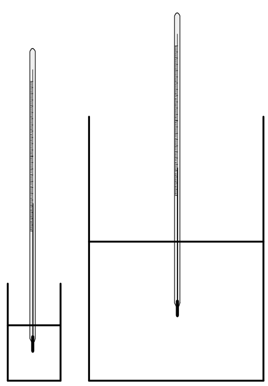
Image you have two glass beakers. Each has a tight fitting glass lid (not something you will actually find in the laboratory –this is a 'thought experiment').
Here are the dimensions of the two beakers:
Beaker 1: height 7 cm, diameter 3 cm
Beaker 2: height 21 cm, diameter 11 cm
Both are filled with boiling water and the lids put on.
Use calculations to support your reasons for drawing the two curves.
Note

- The area of a circle is given by $\pi r^2$, where $r$= the radius of the circle.
- The volume of a cylinder is given by its cross-sectional area x its height.

Sketch cooling curves (temperature against time) to compare the rate at which the water cools in each beaker. You might find it useful to use a mini-whiteboard to make rough sketches. These can be easily erased or modified if your ideas change. When you are happy with the graphs you have drawn, copy them into your notebook.

### Checking your prediction

Now try the following experiment to check your predictions. Of course, you cannot check them precisely since the apparatus is not available. But you can use an experimental set up that will show you whether or not your ideas are reasonable.



You need one 50 $cm^3$ and one 2000 $cm^3$ beaker, two thermometers, a stopwatch and a kettle.

1. Fill each beaker to about two-thirds full with boiling water.
2. Put thermometers into each so that the bulbs are in or close to the middle of the water.
3. Record the temperature every 30 seconds initially and then, after 3 minutes, every 1 minute.
4. Plot a cooling curve (temperature against time) for the water in each beaker.
5. Repeat steps 1-4, but stir the water as it cools.

Explain:

- the shapes of the graphs you obtained
- to what extent your experimental results supported your predictions. (Remember: your investigation did not replicate the 'thought experiment', but it should give you an insight into it.)

## Student sheet: Preparation of azo dyes

The methods below are adapted from "Parallel Combinatorial Synthesis of Azo Dyes" Benjamin W. Gung* and Richard T. Taylor, Journal of Chemical Education, 2004, 81, 1630.
The instructions tell you how to make a range of azo dyes and investigate their usefulness for dyeing various fabrics.

**Health and safety**
Wear protective clothing, including gloves, and safety goggles. A risk assessment must be done before practical work is carried out.

**Equipment and materials**

- depending on the azo dye
  2-aminobenzenesulfonic acid
  3-aminobenzenesulfonic acid
  4-aminobenzenesulfonic acid
- depending on the azo dye
  1-naphthol
  2-naphthol
  2-hydroxybenzoic acid
- sodium nitrite
- 4-nitroaniline
- concentrated hydrochloric acid
- 2.5 mol $dm^{-3}$ sodium hydroxide solution
- saturated sodium chloride solution
- sodium carbonate
- distilled water
- test tubes (three for each dye)
- hot water bath or electric hotplate
- dropping pipettes (two for each dye)
- spatula
- balance
- tweezers
- paper towels
- 25 $cm^3$ conical flasks
- 100 $cm^3$ beakers
- 10 $cm^3$ measuring cylinders
- glass rods
- disposable gloves
- apparatus for filtration under reduced pressure
- scissors
- ruler
- pH meter
- cotton square
- glass funnel
- sodium chloride
- crushed ice
- ice water bath
- SDC Multifibre Strip

### Couplings using diazonium salts of aminobenzenesulfonic acids

*Preparation of the diazonium salt*

Aminobenzenesulfonic acids: 2-aminobenzenesulfonic acid, 3-aminobenzenesulfonic acid and 4-aminobenzenesulfonic acid.

Measure 0.49 g (0.0028 mol) of the aminobenzenesulfonic acid, 0.13 g of sodium carbonate, and 5 $cm^3$ of distilled water into a test tube. Warm the mixture in a water bath to get a clear solution. Remove the test tube from the water bath and add a solution of 0.2 g of sodium nitrite in 0.5 $cm^3$ of water. In a second test tube, place 0.53 $cm^3$ of concentrated hydrochloric acid and 3 g of crushed ice. Add the solution from the first test tube drop by drop to the second test tube. Place the resulting mixture in an ice-water bath to encourage precipitation of the diazonium salts. The suspension formed is used in the next step.

*Coupling reaction*

Coupling compounds: 1-naphthol, 2-naphthol, 2-hydroxybenzoic acid.

Measure 0.0026 mol of the coupling compound into a 25 $cm^3$ conical flask. Add 2 $cm^3$ of 2.5 mol $dm^{-3}$ sodium hydroxide solution. Place the conical flask in an ice-water bath. Add the suspension of the diazonium salt slowly using a dropping pipette, stirring with a glass rod after each addition. Let the reaction continue for 10 minutes, stirring it occasionally. Then heat the suspension on a hotplate or in a hot water bath until the solid dissolves. Add 1 g of sodium chloride and continue heating until it also dissolves. Cool the conical flask to room temperature first and then place it in an ice-water bath. Filter the solid product under reduced pressure. Wash the solid with 2 $cm^3$ of saturated sodium chloride solution. Let it dry in the air. Weigh the product (the azo dye).

*Dyeing a multi-fibre strip*

Caution: Wear disposable gloves.

Dissolve 0.05 g of the azo dye in 20 $cm^3$ of water in a 100 $cm^3$ beaker. Cut a 15 mm strip of multi-fibre material. Put it into the dye solution, making sure it is completely soaked. Keep it immersed and boil the solution for about 5 minutes. Remove from heat with a tweezers and rinse the fibre with tap water. Pat the dyed fibre dry with a paper towel.

### Couplings using diazonium salts of 4-nitrophenylamine

*Preparation of the diazonium salt*

Measure 1.5 $cm^3$ of concentrated hydrochloric acid and 1.5 $cm^3$ of distilled water into a test tube. Place the test tube in an ice-water bath. Measure 0.7 g of 4-nitroaniline, 0.38 g of sodium nitrite and 1.5 $cm^3$ of water into a second test tube. Mix well and cool in an ice-bath. Add the suspension to the first test tube solution at 0 °C using a dropping pipette. Stir the reaction mixture with a glass rod occasionally during the addition and then for a further 10 minutes. Remove any insoluble material by filtration through a small cotton plug in a glass funnel. Collect the filtrate in third test tube.

*Coupling reaction*

Coupling compounds: 1-naphthol, 2-naphthol, 2-hydroxybenzoic acid.

Dissolve 0.0051 mol of one of the coupling compounds in 10 $cm^3$ of 2.5 mol $dm^{-3}$ sodium hydroxide solution in a 25 $cm^3$ conical flask. Place it in an ice-water bath.

Add the diazonium solution from the previous step to the conical flask, drop by drop with stirring. Leave the flask in the ice-water bath for about 10 minutes. Slowly add about 1.5 $cm^3$ of concentrated hydrochloric acid to the mixture until the pH is between 3 and 4. Add 1 g of sodium chloride and heat the conical flask on a hotplate or hot water bath until it is boiling. Cool the mixture to room temperature and then in the ice-water bath. Filter the solid under reduced pressure and wash it with 2-5 $cm^3$ of distilled water. Leave it to dry and weigh the product.

Note: The solution can be used to dye the fabrics directly if no solid is formed.

*Dyeing a multi-fibre strip*
Caution: Wear disposable gloves.

Dissolve 0.05 g of the azo dye in 20 $cm^3$ of water in a 100 $cm^3$ beaker. Add 3 $cm^3$ of 2.5 mol $dm^{-3}$ sodium hydroxide solution and heat the mixture on a hotplate, stirring it with a glass rod.

Cut a 15 mm strip of multi-fibre material. Put it into the dye solution, making sure it is completely soaked. Keeping it immersed, boil in the solution for about 3 minutes. Remove from heat with tweezers and rinse the fibre with tap water. Pat the dyed fibre dry with a paper towel.

## Student sheet: Scaling up

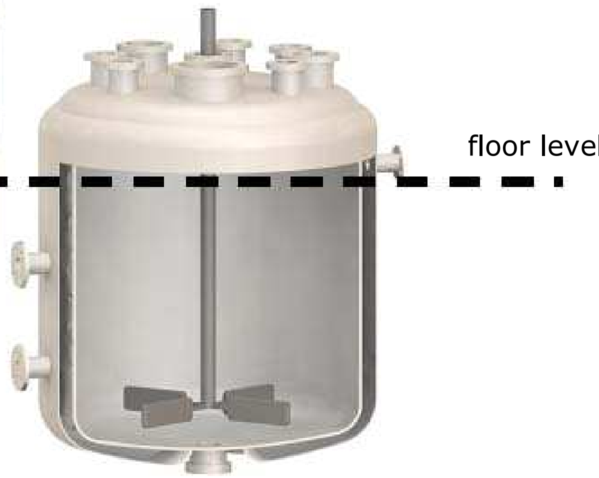
On a large sheet of paper, make a grid similar to the one below.

| **Steps** | **Laboratory apparatus** | **Pilot plant apparatus** | **Key differences** |
|---|---|---|---|
| **Diazonium salt** | | | |
| **Coupling reaction** | | | |

1. Describe the key steps in the preparation of an azo dye in the first column, for the preparation of the diazonium salt and for the coupling reaction.
2. In the second column, put photographs of the relevant piece of laboratory apparatus that you used and name it.
3. Look at photographs of pilot plant equipment. Match these to apparatus you used in the laboratory and put them in the third column.
4. Describe the key differences between laboratory and pilot scale apparatus in the fourth column.

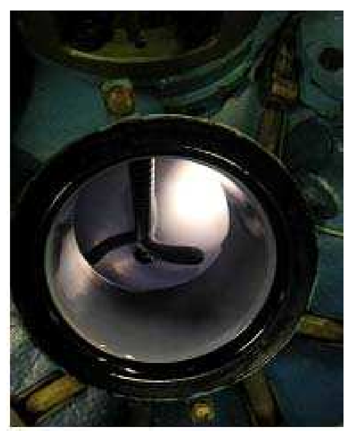
## Student information sheet: Chemical plant


Batch reactors are used to make many chemical substances at pilot plant and at manufacturing scale. The picture below shows a jacketed batch reactor. Heat transfer fluid is pumped around the jacket to keep the inside of the reactor at the required temperature. Reaction mixtures may be heated or cooled in this way.
A heat transfer fluid should have a high specific heat capacity, low viscosity and be cheap.




The picture above shows a large batch reactor for manufacturing chemical substances. There are a number of ports in the top and an electrical motor to drive the stirrer inside the vessel. The top of the reactor is at floor level.

Top of the reactor with a viewing port open



Stirrer seen through the viewing port

The reactor above is a smaller vessel, typically used in pilot plants, though ones of similar size may be used for manufacturing low volume high value products such as certain pharmaceuticals.

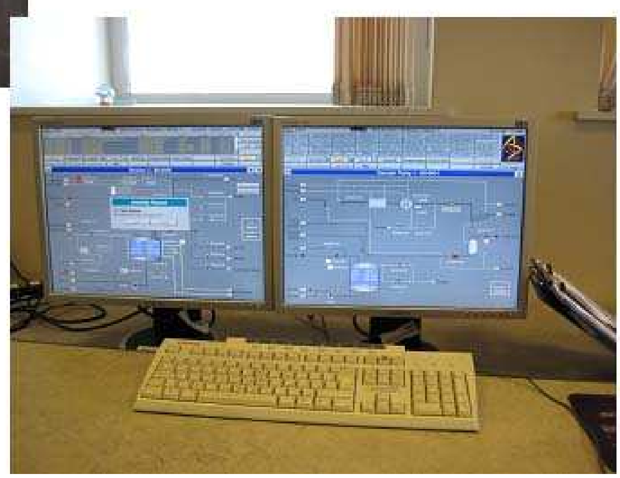


The two pictures above show a solid reactant being weighed and transferred to a small pilot plant batch reactor.

The two pictures below show booths in which solids and liquids are weighed and transferred into large manufacturing batch reactors.


'Solid Charge Booth' from which solids are fed via a hopper into the reaction vessel

'Liquid Charge Booth' from which liquids are pumped from drums into the reaction vessel



Chemical manufacturing process are monitored and controlled by computers

Many products are solids, often precipitated or crystallised from solution. They need to be filtered and dried.

Filtering a crystallised product in a small pilot plant

Drying oven

Drying the product

Filtering a crystallised solid in a large manufacturing plant. The plant has four of these huge filtration vessels running in parallel for one batch.

The 'filter paper' (actually metal gauze) has a diameter of about 1.5 m