

In this activity you will investigate colour changes brought about in a variety of ways, and then identify the type of reaction involved in each case.

Requirements

- 250 cm³ stoppered bottle
- 100 cm³ measuring cylinder
- alkaline solution of glucose (100 cm³)*
- Methylene Blue indicator
- Phenolphthalein and Fluorescein indicators (optional)
- boiling tubes, test-tubes and rack
- acidified solution of ammonium vanadate(V) (ammonium metavanadate, NH₄VO₃) (10 cm³)*
- zinc (granulated)
- zinc oxide (0.5 g)
- Bunsen burner
- lead nitrate(V) (ground to a powder) (0.5g)
- potassium iodide (ground to a powder) (0.5g)
- lead nitrate(V) solution, 0.5 mol dm⁻³ (3 cm³)
- potassium iodide solution, 0.5 mol dm⁻³ (1 cm³)
- teat pipettes
- sodium carbonate solution, 1.0 mol dm⁻³ (1 cm³)
- dilute ammonia solution, 2.0 mol dm⁻³ (5 cm³)
- potassium (or ammonium) thiocyanate solution, KSCN (or NH₄SCN), 0.1 mol dm⁻³ (1 cm³)
- potassium hexacyanoferrate(II) solution, $K_4Fe(CN)_6$, 0.005 mol dm⁻³ (1 cm³)
- dilute solutions (approximately 0.1 mol dm⁻³) containing the following ions (1–2 cm³ of each solution):
 – copper(II)
 - nickel(II)
 - iron(III)
- potassium chromate(VI) solution, 0.5 mol dm⁻³ (2 cm³)
- protective gloves
- dilute sulphuric acid, 1.0 mol dm⁻³ (1 cm³)
- microscope
- slides and coverslips
- rubber bungs
- Universal Indicator solution

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- sodium hydroxide solution, 1.0 mol dm⁻³ (2 cm³)
- small lump of solid carbon dioxide (dry ice) and tongs, or a supply of carbon dioxide
- 250 cm³ beaker

CARE Chromates(VI) irritate the eyes, the skin and the respiratory system. They are also suspected carcinogens. Avoid all skin contact and do not breathe any dust. Any spillage should be washed off at once.

* See instructions for preparation in the Teacher's and Technician's Guide

alkaline solution of glucose





ammonium vanadate(V)

dilute ammonia solution



lead nitrate(V)



Methylene Blue indicator



nickel(II) ion



potassium chromate(VI)



potassium hexacyanoferrate(II)



potassium thiocyanate



sodium hydroxide solution



dilute sulphuric acid

CARE Eye protection and gloves must be worn.



What you do

Investigate the following reactions, which all involve colour changes. In each case, record your observations and try to explain as far as possible what is happening to produce the colour change.

Doing all these reactions takes some time, so you will probably do only *one* of these. Show and explain this reaction to the other members of your class. In a similar way, go round the other members of your class and write down the observations they have made. Use textbooks to help where necessary. You will have met some of the reactions in earlier units (**From Minerals to Elements**, **The Atmosphere** and **The Steel Story**).

Place 100 cm³ of an alkaline solution of glucose (CARE Irritant) in a 250 cm³ bottle with a well-fitting stopper or rubber bung. Add enough Methylene Blue indicator (CARE Harmful) to give a good dark colour to the solution. (Methylene Blue is an indicator whose colour depends on the level of oxygen dissolved in the solution.)

Shake the bottle vigorously and leave it to stand. When the colour of the Methylene Blue has disappeared (this may take up to 30 minutes), shake the bottle again. You can repeat the process many times.

(You can vary the colour change by repeating the experiment and adding Phenolphthalein or Fluorescein as well as Methylene Blue.)

- **2** Place 10 cm³ of acidified ammonium vanadate(V) solution (**CARE** Toxic and an irritant) into a boiling tube and add a piece of granulated zinc. Gently swirl and shake the tube until no further changes occur. You may need to heat the tube gently to speed up the reactions.
- **3** Heat a small sample of zinc oxide in a test-tube until there is no further change in colour. Stand the tube in a rack to cool. When cool, repeat the heating and cooling process.
- 4 Place a spatula-load of powdered lead nitrate(V) crystals into a test-tube. (CARE Lead nitrate(V) is toxic and oxidising. Use only a small amount and do not breathe the dust.) Add a spatula-load of powdered potassium iodide crystals. Cork the tube and shake it vigorously.

Repeat using dilute aqueous solutions of these two substances.

- **5** Investigate what happens when you add the reagent from list **A** to the metal ion solution opposite it in list **B** in Table 1. Use a teat pipette and shake the mixture after each addition. (**CARE** Copper(II) and nickel(II) salts are harmful.)
- **6** Add a few drops of Universal Indicator solution to some water in a beaker. Add enough dilute sodium hydroxide solution to raise the pH and give a deep purple colour. Now add a small lump of solid carbon dioxide (dry ice **CARE** Dry ice should be handled with tongs), or bubble carbon dioxide from a generator through the solution.
- 7 Mix 2 cm³ of lead nitrate(V) solution with 2 cm³ of potassium chromate(VI) solution. (**CARE** Lead compounds are toxic and chromates(VI) are suspected carcinogens. Avoid all skin contact wear gloves.) Put a drop of the resulting mixture on a slide and observe under a microscope.

Repeat the experiment but add a few drops of dilute sulphuric acid (**CARE** Irritant) to the potassium chromate(VI) solution before mixing.

Summary

At the end, draw up a summary table in which you classify each change occurring as one of the following:

- redox reaction
- ionic precipitation reaction
- acid-base reaction
- ligand exchange reaction
- polymorphic change.

(Compounds which can exist in more than one solid form, in which the ions or molecules are arranged in different ways, are said to be **polymorphic**.)

Α	В
sodium carbonate solution	Cu ²⁺ (aq)
ammonia solution	Cu ²⁺ (aq)
ammonia solution	Ni ²⁺ (aq)
potassium hexacyanoferrate(II) solution, K ₄ Fe(CN) ₆ (CARE Harmful)	Fe ³⁺ (aq)
potassium (or ammonium) thiocyanate solution, KSCN (or NH ₄ SCN) (CARE Harmful)	Fe ³⁺ (aq)

Table 1





In this activity you can examine the nature of the light reaching your eye from coloured solutions and from coloured surfaces.

Requirements



What you do.

Point the spectroscope at a window or source of white light and observe the effect it has on the light. (You may wish to use a diffraction grating instead of a spectroscope.)

Investigate the effect of placing a coloured solution between the white light source and the spectroscope, as shown in Figure 1. Summarise your observations in a table.



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Figure 1 Investigating the effect of coloured solutions on white light

Now point the spectroscope at a well-lit brightly coloured surface such as an exercise book or file. You may want to read **Chemical Ideas 6.7** to help you explain your observations.

QUESTIONS _

- a What effect does the spectroscope have on white light?
- **b** Describe what you observed when a coloured solution was placed between the white light source and the spectroscope. Explain why this happens.
- **c** Use your observations with coloured surfaces to help you write a short explanation of why paintings appear coloured when you look at them with the naked eye.





In this activity you will use reflectance spectra to find out which pigments Cima used 500 years ago to produce two different areas of blue in his altarpiece The Incredulity of S. Thomas.

Reflectance spectra

The surface of a painting is not smooth and light is reflected from it in all directions.



paint surface

Figure 1 The reflection of light from a paint surface

A reflectance spectrum tells you how much light of each colour in the spectrum is reflected in a particular direction.

The reflectance spectrum of a painting is obtained by shining light on a small area and analysing the light reflected off the surface of the pigments at a particular angle.

Figure 2 shows a simplified version of the apparatus used. The monochromator contains a prism which splits the white light into its component wavelengths. The prism is rotated so that the wavelength of the light focused on the painting can be varied. The apparatus also incorporates a camera which takes a photograph of the precise spot on the painting that is being examined.



Figure 2 Obtaining the reflectance spectrum of a sample of paint

What you do

Below are the reflectance spectra of two blue pigments used by Cima. They were taken from two different parts of the painting, area A and area B (see Figures 3 and 4). The horizontal axis represents the wavelengths of the light reflected. The vertical axis shows the percentage of the incident light reflected by the pigment.



Study the reflectance spectra in Figures 3 and 4 and then compare them with the reflectance spectra of some traditional blue pigments which were in use at the time Cima was painting the altarpiece. These are shown on **Information**

Sheet 1 (Traditional blue pigments).

QUESTIONS

- **a** Which blue pigments do you think are present in the paint areas A and B?
- b What is the chemical composition of each of these pigments?
- **c** How would you expect the *shade of blue* to differ for the two pigments? (You may want to look at your **Data Sheets** to find out which colours correspond to the various wavelengths in the visible spectrum.)
- **d** Look at Cima's *The Incredulity of S. Thomas* (**Storyline CD4**, Figure 13). Look carefully at the different blue areas in the picture. In which part of the painting do you think Cima might have used these pigments?
- **e** Why do you think it is important to take a photograph of the precise spot on the painting that is being subjected to measurement?
- **f** How might reflectance spectra provide information on the effect of gallery lights on various pigments?

Information Sheet 1: Traditional blue pigments

Pigment	Source	Chemical composition	
Smalt	Zaffre (cobalt arsenate)	Blue glass pigment made by melting cobalt arsenate with sand and K_2CO_3	
Azurite	Azurite	2CuCO ₃ .Cu(OH) ₂	
Natural Ultramarine	Lapis lazuli	A sodium aluminium silicate containing sulphur	
Indigo	Vegetable dye extracted from woad or from the <i>Indigofera</i> <i>tinctoria</i> plant		

Table 1 Information about some traditional blue pigments in use in the early 16th century



Figure 1 Reflectance spectra for four traditional pigments



In this activity you will use information from experiments to decide what factors affect the drying potential of an oil. You can then make some deductions about the complex chemistry of the drying process.

Different types of oil

If a drying oil is exposed to air, it eventually becomes a rubbery solid. If only a thin layer is exposed, it becomes hard. Non-drying oils do not harden in this way, but they may thicken on heating. In between the two extremes are the semi-drying oils. These thicken and form a skin when exposed to air at high temperatures.

Only drying oils are suitable for mixing with pigments to make paints.



Paint layers dry from the outside to give a tacky surface first; eventually they become hard throughout. The drying process is irreversible.

Iodine numbers

Natural oils can be classified according to their iodine number. This is calculated on the basis of how much iodine(I) chloride (ICl) will react with the oil. The more ICl reacts with the oil, the higher the iodine number. Table 1 gives the iodine numbers for some natural oils.

Oil	Drying potential	lodine number
linseed	drying	170–195
рорру	drying	140–158
walnut	drying	140–150
almond	non-drying	<100
olive	non-drying	<100
castor	non-drying	<100
cotton-seed	semi-drying	103–111
maize	semi-drying	117–130
sesame	semi-drying	100–120







A closer look at linseed oil

Figure 2 shows the results of an experiment to investigate the drying of linseed oil. It shows the percentage increase in mass of two samples plotted against the drying time in days. The linseed oil samples were left exposed to the air and were kept at a constant room temperature.

Figure 2 The drying of linseed oil. Curve a is for a film of linseed oil prepared and dried in the dark, and weighed under red light. Curve b is for an identical film of linseed oil prepared, dried and weighed in diffuse daylight. 1 = point of initial set; 2 = tacky stage; 3 = tack-free dryness.



No significant increase in mass was observed if the linseed oil samples were kept in an atmosphere of nitrogen.

- a How is the drying potential of an oil related to its iodine number?
- b Look at the structures of some of the carboxylic acid components of the triesters found in natural oils. You can find these in Chemical Ideas 13.6. With which structural feature of these molecules do you think ICI will react? What *type* of reaction is involved?
- **c** Which parts of the triester molecules in natural oils do you think are involved in the drying process?
- **d** What other substance seems to be involved in the drying reaction? Explain your answer.
- e Suggest what type of chemical processes might be involved when natural oils harden.
- **f** What experiments would you want to do to confirm your suggestions?
- **g** Explain how the drying of an oil paint is different from the drying of watercolours.



Investigating paint media

In this activity you will analyse gas-liquid cbromatograms to find out which oil was used as the binding medium for Cima's paints in The Incredulity of S. Thomas.

The problem

Oils are triesters of glycerol with long-chain carboxylic acids (see **Chemical Ideas 13.6**). Different oils contain different amounts of each acid, and the ratio of the acids can be characteristic of a particular oil.

The trouble is that the cross-linking process which causes paint to dry involves the *unsaturated* carboxylic acid chains, and this polymerisation is irreversible. So, when chemists analyse samples of paint, they measure the ratio of two *saturated* carboxylic acids, since these are not involved in the cross-linking. The acids chosen are *palmitic acid* and *stearic acid*. Their ratio is unchanged by the drying process.

Analysing a sample of paint

A small sample of paint, about the size of a pin head, is removed from the painting and treated to make it suitable for analysis by gas-liquid chromatography (g.l.c.).

First, the paint sample is warmed in potassium hydroxide solution to hydrolyse the ester links in the oil. Potassium salts of the carboxylic acids are produced:

CH ₂ -O-CO R				CH ₂ — OH		R COO ⁻ K ⁺
сн—о—со г '	+	ЗКОН	>	сн—он	+	R 'COO- K+
I СН ₂ —О—СО R "				I CH ₂ — OH		R "COO− K+
oil				glycerol		potassium salts of the carboxylic acids

The groups **R**, **R'** and **R''** vary according to the carboxylic acid present (for palmitic acid, for instance, **R** is $CH_3(CH_2)_{14}$).

The mixture is now acidified with hydrochloric acid to liberate the free carboxylic acids. These will be simple fatty acids as well as acids of the polymeric cross-linked material. Stearic acid and palmitic acids are among the fatty acids produced:

CH₃(CH₂)₁₄COOH CH₃(CH₂)₁₆COOH palmitic acid stearic acid

The free acids are not very volatile and are difficult to analyse using g.l.c. (They take a long time to emerge from the column and do not produce sharp peaks.) The next stage is therefore to convert the acids to their more volatile methyl esters. Because of the very small quantities involved, a powerful methylating agent called *diazomethane* is used:

RCOOH + $CH_2N_2 \longrightarrow RCOOCH_3 + N_2$ diazomethane

It is this mixture of methyl esters which is injected onto the column of the gas-liquid chromatograph. (You can find out how a gas-liquid chromatograph works in **Chemical Ideas 7.6**.)

Figure 1 shows the chromatogram obtained when a small sample of paint from Cima's altarpiece was treated in this way.

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Figure 1 Gas-liquid chromatogram of a sample made from paint from Cima's The Incredulity of S. Thomas.

What you do

Use the information on **Information Sheet 2** (*Gas-liquid chromatograms*) to help you analyse the chromatogram in Figure 1. (The same conditions were used to obtain all the chromatograms.)

First, identify the peaks due to the palmitate and stearate esters, and then work out the palmitate : stearate ratio in the sample. The peaks are very sharp so you can assume that the peak height is proportional to the amount of compound present. (Strictly speaking, you should measure the *area* under each peak.)

Now work out the palmitate : stearate ratios for each of the reference samples, from paint made up in known oils. Compare these ratios with the value you obtained for the sample from Cima's paints.

QUESTIONS

- **a** Which oil do you think was used to bind Cima's paints in 1504? Explain your answer.
- **b** Explain why the palmitate:stearate ratio is the one chosen for analysis.
- **c** Suggest why methyl esters are more volatile than the free carboxylic acids.
- **d** Give another method for converting palmitic acid to its methyl ester. Write a balanced equation for the reaction.

Information Sheet 2: Gas-liquid chromatograms

The conditions used during analysis, the type of chromatography column and detector, the temperature and the flow rate of the carrier gas, were the same in each case. A hydrocarbon with a high relative molecular mass was used as the stationary phase in the column.



Figure 2 Gas-liquid chromatograms of: (a) pure methyl palmitate; (b) pure methyl stearate; (c-f) samples made from paint bound with poppy seed oil, linseed oil, walnut oil and egg tempera, respectively.

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In this activity you can combine evidence from scientific and bistorical sources to identify the yelloworange pigment Cima used for the robe of S. Peter in bis painting The Incredulity of S. Thomas.

What you do.

Your task is to identify the yellow-orange pigment used for the robe of S. Peter. You will use the kind of scientific results and historical information that scientists and art historians at the National Gallery in London had at their disposal when analysing the painting. (S. Peter is the Apostle with the white hair and a beard, standing in the foreground next to Christ on the right-hand side of the picture.)

Photomicrograph of a cross-section of paint

A diagram of this is shown in Figure 1. You may be able to see a coloured slide of it. (A **photomicrograph** is a picture taken under a microscope.)



Figure 1 Diagram of the photomicrograph of a cross-section of paint taken from the robe of S. Peter (x 120)

Historical evidence

Information Sheet 3 (*Background information on some yellow pigments*) gives some historical information about the use of yellow and orange pigments. These extracts are taken from a standard textbook on painting materials. Such information is always used in addition to the results of any scientific analysis.

LMA emission spectrum

The **emission spectrum** from the paint sample consists of a series of lines. It is projected onto a reference spectrum in a special apparatus. The elements present in the sample are then identified by matching the lines to those on the reference spectrum.

The LMA emission spectrum of the yellow-orange pigment from S. Peter's robes showed characteristic lines at 228.8 nm and 235.0 nm. You can see a small section (from 223 nm to 252 nm) of the reference spectrum in Figure 1 on **Information Sheet 4** (*Reference emission spectrum for LMA spectra*). The apparatus at the National Gallery could detect light emitted between 220 nm and 460 nm (i.e. ultraviolet and visible light) so the whole reference spectrum is very long!

Summary

Write a *short* report summarising your findings. Which pigment do you think Cima used? Give reasons for your decision.

Information Sheet 3: Background information on some yellow pigments

Barium Yellow This is barium chromate(VI), $BaCrO_4$. It is a pale green-yellow pigment made by mixing neutral solutions of potassium chromate(VI) and barium nitrate(V). It may become slightly greener on exposure to light due to formation of chromium(III) oxide. The metal chromium was discovered by Vauquelin in 1797 and he described the preparation of barium chromate(VI) in 1809.

Cadmium Yellow This is cadmium sulphide, CdS, which is prepared by precipitation from an acid solution of a soluble cadmium salt (chloride or sulphate) with hydrogen sulphide or an alkali metal sulphide. The colour of pure cadmium sulphide ranges from lemon yellow to deep orange, depending on the way it is prepared. Cadmium sulphide exists naturally as the mineral *Greenockite*, but the use of the mineral as a pigment has not been recorded.

The first chemical preparation of cadmium sulphide seems to have been by Stromeyer in 1817. It is now perhaps the most important yellow pigment in the artist's palette, though there are increasing concerns about its toxic nature.

Chrome Yellow (See **Storyline CD3**.) This is lead chromate(VI), PbCrO₄. It is a bright yellow pigment made by mixing solutions of potassium chromate(VI) and lead nitrate(V). Vauquelin described its preparation by this method in 1809; a range of different shades of yellow may be produced depending on the conditions.

Indian Yellow This is a yellow organic extract introduced in the 15th century. It was prepared at Monghyr in Bengal from the urine of cows fed on mango leaves. Its manufacture by this method is now prohibited by law. It has a deep, rich, translucent, orange colour. This pigment was used in India in the manufacture of paint because of its resistance to fading when exposed to light. The colour sold under this name today is a synthetic substitute.

Lead-Tin Yellow X-ray crystallography has shown this pigment to be an artificially produced compound of the oxides of tin and lead containing silicon as an essential constituent, PbSnSiO₃.

Recipes in the Bolognese Manuscript of the early 15th century note the manufacture of 'yellow glass for beads' involving heating lead and tin together in a furnace, followed by a second stage to produce a pigment for painting. Lead-Tin Yellow was used extensively in Venetian 16th century painting and continued to be used into the mid-17th century.

Naples Yellow This is lead antimonate. It may be considered to be chemically combined lead and antimony oxides, $Pb_3(SbO_4)_2$. It varies in colour from sulphur-yellow to orange-yellow. Recipes for it first appeared in the 18th century.

Orpiment This was once widely used as a pigment, particularly in the East, but has now fallen into complete disuse because of its limited supply and its poisonous nature. It is the yellow sulphide of arsenic, As₂S₃, occurring naturally in many places but not in large quantities. Orpiment is brilliant when pure, with a rich lemon-yellow tone. It is mentioned as a pigment in 14th and 15th century Italy, and although quite rare elsewhere, it is characteristic of many 16th century Venetian paintings.

Realgar This is a natural orange-red sulphide of arsenic, As_2S_2 , and is closely related chemically to Orpiment. The two minerals are often found together in the same deposits. Like Orpiment it was known in ancient times.

Yellow Ochre An *ochre* is a natural earth pigment which consists of a mixture of silica and clay. It owes its colour to the presence of iron(III) oxide, Fe_2O_3 . In Yellow Ochre, the colour is caused by the presence of various hydrated forms of the oxide. Yellow Ochre has been used universally as a pigment from earliest history. It was known and used in ancient Egypt, in Roman times and in the East. It was important in the Middle Ages and in all periods of European painting.



Information Sheet 4: Reference emission spectrum for LMA spectra

The reference spectrum is an emission spectrum of iron which has many lines throughout the 200 nm-460 nm range. The full reference spectrum is very long and has marked on it the positions of the characteristic lines of around 60 elements.

Below is a small section of the reference spectrum, between 223 nm and 252 nm.



Figure 1 A small section (from 223 nm to 252 nm) of the reference spectrum for use with LMA emission spectra of pigments. (The upper spectrum is a spark spectrum; the lower one an arc spectrum.)



In this activity you will use reflectance spectra to find modern replacements for two blue pigments used in Cima's The Incredulity of S. Thomas.

Why use modern pigments?

Why don't restorers simply use the original pigments once these have been identified?

Restorers may substitute modern pigments for several reasons. It may be that the original pigment is not available, or that the modern version of it is not quite the same. Immense care was taken with the preparation of pigments in the workshops of Renaissance artists. The chemically equivalent pigments available today rarely give as intense a colour. In addition, the original pigment may have changed colour with age.

Modern pigments are readily available. They are usually more stable and less toxic than their traditional counterparts.

Although it is often possible to match a modern colour exactly to that of a faded original pigment, it is not possible to ensure that the two pigments will change in the same manner in the future. There is no point in achieving a perfect match with an old pigment only to see the retouching fade. One solution is to keep the restored painting in a carefully controlled environment, so that all further change is kept to a minimum.

What you do.

Imagine you are a scientist working in the Scientific Department at the National Gallery. You have just received a memo from the Conservation Department asking you to recommend the best blue pigments for use in the restoration of two areas of Cima's altarpiece:

- the blue-green areas of the ceiling
- the dark blue mantle of the Apostle on the extreme left of the group.

You have already supplied the Department with the identity of the original pigments used by Cima (look back to **Activity CD4.1**). Now you need to find the best modern substitutes.

The reflectance spectra of some modern blue pigments are shown on **Information Sheet 5** (*Some modern blue pigments*). Use these spectra to help you construct a reply to the Conservation Department. Outline the reasons for your recommendations.

Information Sheet 5: Some modern blue pigments



Figure 1 Reflectance spectra of some modern blue pigments

CD5 Comparing hydrocarbons

The purpose of this activity is to compare the behaviour of three liquid hydrocarbons – cyclobexane (an alkane), cyclobexene (an alkene) and methylbenzene (an arene) – with a series of chemical reagents.

Requirements

- test-tubes and rack
- bungs
- boiling tube
- teat pipettes
- cyclohexane (2 cm³)
- cyclohexene (2 cm³)
- methylbenzene (2 cm³)
- bromine in cyclohexane solution (3 cm³)
- glass rod
- concentrated ammonia solution (2 cm³)
- bromine water (6 cm³)
- concentrated nitric acid (2 cm³)
- concentrated sulphuric acid (fresh) (7 cm³)
- dilute sulphuric acid, 1.0 mol dm⁻³ (20 cm³)
- dilute potassium manganate(VII) solution, 0.02 mol dm⁻³ (3 cm³)
- potassium manganate(VII) crystals (0.5g)
- solid sodium carbonate (0.05 g)
- sodium disulphite(IV) (metabisulphite) solution, 1.0 mol dm⁻³ (5 cm³)
- 250 cm³ beaker
- 10 cm³ measuring cylinder
- 100 cm³ conical flask
- 0–110 °C thermometer
- source of hot water
- crushed ice (50 g)
- methyl benzoate (2.5 cm³)

CARE Cyclohexane, cyclohexene and methylbenzene are highly flammable liquids. Keep bottles stoppered when not in use and well away from naked flames. Avoid skin contact and do not breathe the vapours.

CARE Bromine is corrosive, causes severe burns and gives off a toxic vapour. Handle the bromine solution with care. Measure out in a fume cupboard using a marked pipette.

CARE Solid potassium manganate(VII) is a powerful oxidising agent. It causes staining of skin and clothes. Wear protective gloves if necessary.

concentrated ammonia solution

concentrated nitric acid

bromine water

bromine



CORROSIVE

COBBOSIVE

concentrated sulphuric acid







cyclohexene

dilute sulphuric acid







methyl benzoate

methylbenzene



potassium manganate(VII) crystals

X

sodium carbonate

sodium disulphite(IV) solution



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Introduction

Arenes have characteristic properties which are very different from those shown by alkanes and alkenes. In this activity you will compare the reactions of cyclohexane (an alkane), cyclohexene (an alkene) and methylbenzene (an arene). (Benzene itself is toxic and has carcinogenic properties, so it cannot be used.)



What you do_

For each of the test-tube reactions, use just a *few drops* of each of the hydrocarbons.

In each case, think first what you expect to happen and why. Then compare this with what you actually observe.

Describe what happens in each case. Write equations where appropriate, and name the products of any reactions. It may be best to draw up tables for your results. You may wish to consult **Chemical Ideas** Chapter 12 to help you interpret your observations.

Classify the *type* of reaction occurring, choosing words from the list below:

substitution	nucleophilic
addition	electrophilic
oxidation	radical

1 Reaction with bromine

- 1 For each hydrocarbon in turn (**CARE** Highly flammable liquids with harmful vapours), place a few drops in a test-tube and add 1 cm³ of a solution of bromine in cyclohexane (**CARE** Corrosive and gives off a toxic vapour). Stopper the tubes and shake them thoroughly. Test any gases given off by holding a drop of ammonia solution (**CARE** Corrosive) on a glass rod at the mouth of the test-tube.
- 2 Repeat the tests in step 1, but this time add a few cm³ of bromine water (CARE Irritant) to each tube.

2 Reaction with potassium manganate(VII)

3 Mix 3 cm³ dilute sulphuric acid (**CARE** Irritant) and 3 cm³ dilute potassium manganate(VII) solution in a test-tube.

Add 1 cm³ of the above solution to a few drops of each hydrocarbon in separate test-tubes. Stopper the tubes and shake them thoroughly.

If no reaction occurs, carefully warm the tube (by placing it in a beaker of warm water) and then leave it to stand.

4 Investigate the reaction with methylbenzene further, as follows. Put 5 drops of methylbenzene (**CARE** Highly flammable liquid with harmful vapour), 5 cm³ of water, 0.05 g of solid sodium carbonate (**CARE** Irritant) and 0.5 g of potassium manganate(VII) crystals (**CARE** Powerful oxidising agent, harmful) into a boiling tube.

Clamp the tube in a near-vertical position and lower it into a beaker of water. Heat the water until the contents of the boiling tube start to reflux. Continue heating gently until the purple colour of the manganate(VII) ions disappears. (Alternatively, a small-scale reflux apparatus with a pear-shaped flask and a water condenser could be used. The flask could be carefully heated with a small Bunsen flame.)

Cool the mixture and then acidify by adding dilute sulphuric acid (**CARE** Irritant). Add sodium disulphite(IV) (metabisulphite) solution (**CARE** Harmful) to remove the brown manganese(IV) oxide.

Use a textbook to find out the name of the white crystals formed, and to help you explain what has happened.



3 Nitration of methyl benzoate

One of the most important reaction of arenes is **nitration**. For example:



The nitro-derivatives of methylbenzene can be explosive. For example:



is trinitrotoluene (TNT; toluene is the old name for methylbenzene). A safer compound to nitrate is methyl benzoate:



5 Measure 2.5 cm³ of methyl benzoate (**CARE** Harmful) into a small conical flask and then add 5 cm³ of concentrated sulphuric acid (**CARE** Corrosive). When the liquid has dissolved in the acid, cool the mixture in ice.

Prepare the *nitrating mixture* by carefully adding 2 cm³ of concentrated sulphuric acid (**CARE** Corrosive) to 2 cm³ of concentrated nitric acid (**CARE** Corrosive; oxidising agent). Cool the mixture in ice during the addition.

Now add the nitrating mixture drop by drop from a teat pipette to the solution of methyl benzoate while cooling. (Do not allow the nitrating mixture to get into the rubber teat.)

Stir the mixture with a thermometer and keep the temperature below 10 °C. When the addition is complete, allow the mixture to stand at room temperature for another 15 minutes.

After this time, pour the reaction mixture onto about 25 g of crushed ice and stir until the ice has melted.

QUESTIONS

- **a** You used cyclohexane and cyclohexene as examples of a typical alkane and alkene respectively. Why weren't simpler hydrocarbons such as ethane and ethene used?
- **b** In the reactions with bromine water and acidified potassium manganate(VII) solution, why was it necessary to shake the tubes thoroughly?
- **c** How would you expect benzene to react with an acidified solution of potassium manganate(VII)? Explain your answer.
- **d i** In the nitration of methyl benzoate, what precautions were taken to help prevent further nitration to a dinitro-derivative?
 - ii Give the names and structural formulae of two nitro-compounds that are likely to contaminate the crystals of methyl 3-nitrobenzoate that you made.
 - iii Suggest how you could purify your crystals and confirm that they are crystals of methyl 3-nitrobenzoate.



In this activity you can investigate the range of colours which can be obtained by making azo dyes with different coupling agents.

Requirements



Azo dyes

Azo dyes are produced in a diazo coupling reaction. For example,



where **R** and **R**' are arene groups and **Z** is a functional group such as -OH or $-NH_2$. When **Z** is an -OH group, the coupling agent is prepared in alkaline solution.

Many modern azo dyes are formed directly on the fibres. First the cotton material is dipped into a solution of the coupling agent. The material is almost colourless at this stage. Next the cotton is treated with an ice-cold solution of a diazonium salt made from an arylamine. The insoluble dye is trapped in the fibres.

What you do_____

Your group will work as a 'development team'. You will prepare a series of azo dyes with different R'Z groups to investigate the range of colours that can be produced.



This means that you will use the same diazonium salt in each reaction and vary the coupling agent. You can select your amine RNH_2 to make the diazonium salt, and the coupling agents (HR'Z) from those in the table below.



* indicates the position where coupling is most likely to occur

Making the diazonium salt

- **1** First make a stock solution of a diazonium salt. Measure out your chosen amine (RNH_2) into a boiling tube. Use 0.15 cm^3 (about 2–3 drops) of phenylamine (**CARE** Toxic) or 0.25 g of benzocaine. Add 10 cm³ of dilute hydrochloric acid and swirl the solution to ensure mixing.
- **2** Cool the solution by placing the tube in a beaker containing an ice-salt mixture, until the temperature of the solution is just below 5 °C. (If the temperature falls too low, the contents of the tube will freeze.)
- **3** Meanwhile, prepare a solution of 2 g of sodium nitrite (nitrate(III)) (**CARE** Toxic; oxidiser) in 10 cm³ of water in another boiling tube. Swirl to ensure mixing and cool this solution to 5 °C.
- **4** Add the sodium nitrite solution *slowly* to the amine salt solution with stirring, taking care that the temperature does not rise above 5 °C. Continue adding the sodium nitrite solution until the mixture gives an instantaneous blue-black colour when spotted on starch-iodide paper. This indicates that diazotisation is complete and excess nitrous acid is present.

The diazonium salt solution is now ready for use. It should be kept cold.

The diazo coupling reaction

5 Dissolve a few crystals (or drops) of your chosen coupling agent in 2 cm³ of dilute sodium hydroxide solution. Cool this solution to 5 °C. Add 2 cm³ of cold diazonium salt solution drop by drop and stir. After noting your results, dispose of the products down the sink with lots of water.

Looking at your results

A2 LEVEL

Draw out the structures of the dyes you have made and identify the chromophore in each. Note the colour of each dye. Highlight parts of the molecules which are the same and those which are different. How did the nature of R' and Z affect the colour of the dye?

Compare your results with a group who have used a different diazonium salt in their coupling reactions. How did the nature of R affect the colours of the dyes produced?

Given time and chemicals, what other compounds would you choose to make? What colours would you expect them to be?

QUESTIONS

- **a** Write out equations for the formation of the dyes you have made.
- b Why is it essential to keep the diazonium salt solution below 5 °C?
- c When phenol dissolves in sodium hydroxide solution, sodium phenoxide is formed. Write down its formula. Suggest why this is used in the coupling reaction rather than phenol itself.



Dyeing with a direct dye and a reactive dye

In this activity you will dye cotton cloth with a fibrereactive dye and with a direct dye, and then compare the fastness to washing.

Requirements

- samples of untreated white cotton cloth (about 5 g each) (2)
- protective gloves
- 400 cm³ beakers (2)
- Durazol Red 2B solution (a direct dye) (250 cm³)*
- Procion Red MX-5B solution (a reactive dye) (200 cm³)*
- sodium chloride (13 g)
- sodium carbonate (0.5g)
- stirring rods
- tongs
- soap powder
- strip chromatography paper
- beaker to use as chromatography tank
- Bunsen burner, tripod and gauze
- * See instructions for preparation in the Teacher's and Technician's Guide

What you do

You are given instructions for dyeing cotton cloth with two different dyes, a fibre-reactive dye and a direct dye.

Dye samples of white cotton with the two dyes and then compare their fastness to washing. While you are dyeing the cotton samples, you can investigate the hydrolysis of the reactive dye in the dyebath using chromatography.

Dyeing cotton with a direct dye

1 First make up the dyebath. Put 250 cm³ of Durazol Red 2B solution (**CARE** Irritant) into a 400 cm³ beaker and add 1 g of sodium chloride. Heat until boiling. Immerse the cotton cloth in the dyebath and continue heating for 10 minutes with occasional stirring. Remove the cloth and rinse it thoroughly with water.

Dyeing cotton with a reactive dye

- **2** Put 200 cm³ of Procion Red MX-5B solution (**CARE** Irritant) into a 400 cm³ beaker. Immerse the cotton cloth and then add 12 g of sodium chloride in small amounts over 5 minutes. Leave the mixture to stand for 10 minutes, stirring from time to time. Then add 0.5 g of sodium carbonate and stir until dissolved.
- **3** Continue the dyeing with occasional stirring for a further 30 minutes. Remove the cloth and rinse it well with water. Finally, wash the cloth thoroughly in hot soap solution.



Procion Red MX-5B



sodium carbonate

CARE Eye protection must be worn.

CARE Avoid all skin contact with the dyes. Gloves must be worn.





How much dye is hydrolysed?

One problem with fibre-reactive dyes is that they are hydrolysed in solution. The dye breaks down and the *dicblorotriazinyl* group, which attaches the dye to the fibre, is lost.

You can investigate the extent of the hydrolysis reaction using chromatography. Chromatography paper reacts with the dye in a similar way to cotton. Both are made of cellulose.

4 Put a spot of the Procion Red MX-5B dye solution (containing sodium chloride) onto a strip of chromatography paper. Leave for 10 minutes and then add a drop of concentrated sodium carbonate solution to the spot. Stand the paper in a 1 cm depth of water in a beaker, making sure the water level is *below* the spot. Allow the water to rise up the paper. The dye which has reacted with the paper will not move. Any hydrolysed dye will move up the paper with the water.

Fastness testing

5 Devise a procedure for testing your dyed samples for fastness to washing. Remember that when clothes are washed, it is important that the colours do not fade, and also that colours are not transferred from one garment to another. The instructions on a packet of washing powder will give you an idea of the conditions suitable for testing fastness to washing.

Results

- **6** Write a short report summarising your findings. It should include the following points:
 - How did the appearance of the two samples of dyed cloth compare?
 - What are the advantages and disadvantages of each dyeing process?
 - How did fastness to washing of the two dyes compare?

Be prepared to make an oral presentation of your results. Compare your findings with those of other groups.



Different dyes for different fibres

This activity demonstrates how a knowledge of the structure of dyes and fibres enables chemists to dye successfully a wide variety of fabrics.

Requirements



What you do.

You are provided with a mixture of three dyes. First, you will use the dye mixture to dye three types of fabric as described below. Different fibres have different structures and bind dyes to different extents.

You can then investigate the composition of the dye mixture using chromatography.

Finally, you will use your observations, together with your knowledge of fibres and how dyes bind to fibres, to assign structures to each of the dyes in the mixture.

Dyeing different fabrics with the dye mixture

- **1** Dilute 10 cm³ of the dye mixture (**CARE** Irritant) to 100 cm³ with water. Heat the solution to boiling in a 400 cm³ beaker. Add small strips of white cotton, polyester and nylon. Avoid using fabrics with a mixed composition.
- **2** Allow the pieces of fabrics to boil gently in the dye solution for 10–15 minutes. Remove the samples with tongs, rinse well with cold water and allow to dry. Note the colour of the various fabrics.

What's in the dye mixture?

3 Investigate the composition of the dye mixture using paper chromatography, with a 95% butanol : 5% water mixture as the solvent (**CARE** Flammable and harmful).

Which dye is which?

The three dyes in the mixture have the following structures, X, Y and Z.



4 Use your knowledge of how dyes bind to fibres, together with your observations, to assign structures X, Y and Z to each of the three dyes in the mixture. Explain your reasoning.

Remember that paper is a cellulose polymer made up of glucose units, like cotton. You made need to look back to **Designer Polymers** for the structure of nylon and polyester fibres. Polyesters are relatively non-polar. Water does not penetrate the fibres well and the fabric is best dyed with small, relatively non-polar molecules. The main attractive forces between the dye molecules and the polyester fibres are instantaneous dipole–induced dipole forces. Nylon too has non-polar sections in its fibres, but also has $-NH_3^+$ groups at the end of the chains in acid solution.

What's the use?

5 Suggest ways in which a textile manufacturer might use a dye mixture of this type.



Check your notes on Colour by Design

This activity belps you get your notes in order at the end of this unit.

Use this list as the basis of a summary of the unit by collecting together the related points and arranging them in groups. Check that your notes cover the points and are organised in appropriate ways.

Most of the points are covered in the **Chemical Ideas**, with supporting information in the **Storyline** or **Activities**. However, if the *main* source of information is the Storyline or an Activity, this is indicated.

- The absorption of ultraviolet light and visible light in terms of transitions between electronic energy levels.
- The use of ultraviolet (u.v.) and visible spectroscopy to help identify unsaturated organic molecules.
- Colour changes associated with the following types of chemical changes: acid–base (indicators), ligand exchange, redox, precipitation and polymorphism (different crystal structures).
- The relation between the properties of pigments (colour shade, colour density, fastness, resistance to atmospheric pollution) to relevant chemical properties (**Storyline CD2** and **CD3**).
- The general principles of gas-liquid chromatography (g.l.c.).
- The techniques used to identify the materials used in a painting, including the use of g.l.c., atomic emission spectroscopy, and visible spectroscopy (reflection and transmission) (**Storyline CD3** and **CD4**; **Activities CD4.1–4.5**).
- The nature of fats and oils as mixed esters of propane-1,2,3-triol with varying degrees of unsaturation.

- An outline of the process of oxidative cross-linking by which unsaturated oils harden; the relationship of this process to their use as media in oil-based paints.
- What arenes and arene derivatives (aromatic compounds) are.
- The structure of benzene.
- How the characteristic properties of aromatic compounds arise from the delocalisation of electrons.
- The following electrophilic substitution reactions of arenes: halogenation of the ring, nitration, sulphonation, Friedel-Crafts alkylation and Friedel-Crafts acylation.
- The formation of azo dyes by coupling reactions involving diazonium compounds.
- The structure of a dye molecule in terms of its various components: chromophore, groups which modify the chromophore, groups which made the dye more soluble in water and groups which attach the dye to the fibre (**Storyline CD5–CD7**).
- Ways in which dyes attach themselves to fabrics: weak intermolecular forces, hydrogen bonds, ionic attractions and covalent bonding (**Storyline CD7**; **Activity CD7.2**).
- The relationship between the colour of a dye and the presence of a chromophore, and groups that modify the chromophore, in the dye molecule.
- The relationship between colour in materials and transitions between electronic energy levels.