Experimental Techniques and Analysis

Apparatus and experimental design, acid–base titrations, paper chromatography and Rf values, separation and purification methods, and the tests for anions, cations, gases and flame colours.

12.1 Experimental design

Apparatus

Apparatus	Used to measure	Notes
stop-watch	time	digital ones measure to $0.01\ \text{s}$
thermometer	temperature	
balance	mass	
burette	a **variable** volume of liquid, accurately	used in titrations; read the bottom of the meniscus at eye level
volumetric pipette	one **fixed**, exact volume (such as $25.0\ \text{cm}^3$)	more accurate than a measuring cylinder
measuring cylinder	an approximate volume of liquid	quick, but less accurate than a burette or pipette
gas syringe	the volume of a gas	more accurate than collecting over water

When you are asked to **suggest the advantages and disadvantages** of a method or apparatus, think about **accuracy** (how close to the true value), **how easy it is to use**, **the time taken**, **safety** and **whether anything is lost** (for example a gas escaping while a bung is put in).

Definitions

- A **solvent** is a substance that **dissolves** a solute.
- A **solute** is a substance that is **dissolved** in a solvent.
- A **solution** is a **mixture** of one or more solutes dissolved in a solvent.
- A **saturated solution** contains the **maximum concentration of solute** dissolved in the solvent **at a specified temperature**.
- A **residue** is a substance that **remains after** evaporation, distillation, filtration or a similar process.
- A **filtrate** is the **liquid or solution that has passed through** a filter.

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12.2 Acid–base titrations

A **titration** finds the exact volume of one solution that reacts with a measured volume of another.

Method.

1. Use a **volumetric pipette** to put exactly $25.0\ \text{cm}^3$ of the alkali into a **conical flask**.
2. Add a few drops of a suitable **indicator** (for example methyl orange, or thymolphthalein).
3. Fill the **burette** with the acid and note the **initial reading**.
4. Add the acid to the flask, **swirling** it, and go **drop by drop** as the end-point is near. Stand the flask on a **white tile** to see the colour change clearly.
5. Stop at the **end-point**: the first **permanent** colour change of the indicator.
6. Note the **final reading**. The **titre** is the final reading minus the initial reading.
7. **Repeat** until you have two or more results that agree closely (within $0.10\ \text{cm}^3$, called concordant results), and **take the mean** of them.

Indicator	Alkali in the flask	End-point colour change
methyl orange	yellow	yellow ⟶ orange/red
thymolphthalein	blue	blue ⟶ colourless

The **end-point** shows when the amounts of acid and alkali are exactly in the ratio given by the equation, so the result can be used to calculate a concentration (see chapter 3).

12.3 Chromatography

Paper chromatography separates a mixture of **soluble** substances, for example the dyes in an ink or food colouring.

Method.

1. Draw a **baseline in pencil** on the chromatography paper. (Pencil is used because ink would dissolve in the solvent and run.)
2. Put a small **spot** of each substance on the baseline.
3. Stand the paper in a container with a **suitable solvent**, with the **solvent level below the baseline**.
4. The solvent **rises up the paper** and carries the substances with it. Each substance moves a **different distance**, because they differ in how **soluble** they are in the solvent and how strongly they are attracted to the paper.
5. Remove the paper before the solvent reaches the top, and mark the **solvent front** at once.

Colourless substances can be shown using a **locating agent**, a chemical that is sprayed on the dry paper and reacts with them to make coloured spots. (Knowledge of specific locating agents is not required.)

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Interpreting a chromatogram

- A **pure** substance gives **one spot**. An **impure** substance (a mixture) gives **two or more spots**.
- Two substances are **the same** if their spots travel the **same distance** in the same solvent. An **unknown** can be identified by comparing its spots with those of **known substances** on the same paper.

$$R_f = \frac{\text{distance travelled by the substance}}{\text{distance travelled by the solvent}}$$

Both distances are measured from the **baseline**, and the substance's distance is to the **centre of its spot**. R_f has **no units** and is always **between** 0 **and** 1.

TRY IT

On a chromatogram a spot is $3.2\ \text{cm}$ above the baseline and the solvent front is $8.0\ \text{cm}$ above it. Find the R_f value.

$R_f = \frac{3.2}{8.0} = 0.40$

12.4 Separation and purification

The method of separating a mixture depends on the **physical properties** of its parts.

Method	Separates	Example
a suitable solvent	a mixture of a soluble and an insoluble solid, by dissolving one of them	salt and sand: add water, which dissolves the salt only
filtration	an **insoluble solid** from a liquid	sand from water
crystallisation	a **soluble solid** from its solution, by evaporating some of the solvent, then cooling to form crystals	copper(II) sulfate crystals from copper(II) sulfate solution
simple distillation	a **solvent from a solution**, or a liquid from a mixture with large differences in boiling points	pure water from salt water
fractional distillation	**miscible liquids** that have **different boiling points**	ethanol from water; the fractions of petroleum; gases from liquid air

Simple distillation. The solution is heated, the solvent boils and its vapour passes into a **condenser**, where it is cooled and **condenses** into the pure liquid, which is collected. The **solute stays** in the flask. In the condenser, cooling water goes in at the **bottom** and out at the **top**, so that the jacket stays full.

Note Academy

Fractional distillation. A **fractionating column** (packed with glass beads) is between the flask and the condenser. The liquid with the **lower boiling point** reaches the top of the column first and distils over. The liquid with the higher boiling point stays in the column and flask until the temperature rises. The thermometer shows the boiling point of the substance that is distilling.

Choosing a method. Decide what is in the mixture, whether each part is soluble or insoluble, and whether the parts have different boiling points.

> TRY IT
>
> Describe how to obtain pure water and dry salt crystals from a mixture of sand, salt and water.

Filter the mixture. The sand is the **residue** and the salt solution is the **filtrate**. Then either use **simple distillation** to collect the pure water, and the salt remains in the flask, or **heat the filtrate** in an evaporating basin to evaporate some water, leave it to **crystallise**, and filter and dry the salt crystals.

Purity

A **pure** substance has a **sharp melting point and boiling point**, at the same temperature each time. If the melting point is **lower** than the known value, or if it **melts over a range**, the substance is **impure**. The same is true for a boiling point, which is **higher** if the liquid is impure.

Note Academy

12.5 Identification of ions and gases

Tests for anions (negative ions)

Ion	Test	Positive result
carbonate, CO_3^{2-}	add **dilute acid**	**effervescence**. The gas turns **limewater milky** (carbon dioxide)
chloride, Cl^-	acidify with **dilute nitric acid**, then add **aqueous silver nitrate**	**white** precipitate
bromide, Br^-	as above	**cream** precipitate
iodide, I^-	as above	**yellow** precipitate
nitrate, NO_3^-	add **aqueous sodium hydroxide**, then **aluminium foil**, and **warm**	**ammonia** gas is given off (it turns **damp red litmus paper blue**)
sulfate, SO_4^{2-}	acidify with **dilute nitric acid**, then add **aqueous barium nitrate**	**white** precipitate
sulfite, SO_3^{2-}	add **acidified aqueous potassium manganate(VII)**	the purple colour is **decolourised** (turns colourless)

NOTE

The solution is **acidified first** (with dilute nitric acid) so that the **carbonate** ions, which would also make a precipitate, are removed, and only the halide or sulfate ions give a precipitate.

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s) \qquad Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$$

Tests for cations (positive ions)

Add **aqueous sodium hydroxide** drop by drop, then in excess. In another test, do the same with **aqueous ammonia**.

Note Academy

Cation	Aqueous sodium hydroxide	Aqueous ammonia
aluminium, Al^{3+}	**white** precipitate, **soluble in excess** (colourless solution)	white precipitate, **insoluble in excess**
ammonium, NH_4^+	no precipitate. **Ammonia** gas is given off when **warmed**	no precipitate
calcium, Ca^{2+}	**white** precipitate, **insoluble in excess**	no precipitate (or a very slight white precipitate)
chromium(III), Cr^{3+}	**green** precipitate, **soluble in excess**	**grey-green** precipitate, **insoluble in excess**
copper(II), Cu^{2+}	**light blue** precipitate, **insoluble in excess**	light blue precipitate, **soluble in excess** giving a **dark blue solution**
iron(II), Fe^{2+}	**green** precipitate, **insoluble in excess** (turns brown at the surface on standing)	**green** precipitate, **insoluble in excess**
iron(III), Fe^{3+}	**red-brown** precipitate, **insoluble in excess**	**red-brown** precipitate, **insoluble in excess**
zinc, Zn^{2+}	**white** precipitate, **soluble in excess** (colourless solution)	white precipitate, **soluble in excess** (colourless solution)

TRY IT

A solution gives a white precipitate with aqueous sodium hydroxide that dissolves in excess. With aqueous ammonia, the white precipitate also dissolves in excess. Which cation is present?

White precipitate soluble in excess of **both** reagents is **zinc**, Zn^{2+}. (Aluminium does not dissolve in excess ammonia.)

Note Academy

Tests for gases

Gas	Test	Positive result
ammonia, NH_3	**damp red litmus paper**	turns **blue**
carbon dioxide, CO_2	bubble through **limewater**	turns **milky** (cloudy)
chlorine, Cl_2	**damp litmus paper**	**bleached** (turns white)
hydrogen, H_2	a **lighted splint**	a **squeaky pop**
oxygen, O_2	a **glowing splint**	the splint **relights**
sulfur dioxide, SO_2	**acidified aqueous potassium manganate(VII)**	the **purple colour is decolourised** (turns colourless)

Flame tests

Dip a clean **nichrome or platinum wire** (cleaned with hydrochloric acid) into the sample and hold it in a **blue Bunsen flame**. The flame colour identifies some **metal ions**.

Cation	Flame colour
lithium, Li^+	**red**
sodium, Na^+	**yellow**
potassium, K^+	**lilac**
calcium, Ca^{2+}	**orange-red**
barium, Ba^{2+}	**light green**
copper(II), Cu^{2+}	**blue-green**

Note Academy