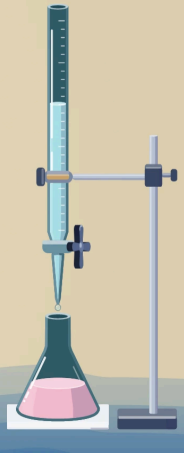
LEARNERS' ALLEY
Designed by Khow Willard

7 Practical Chemistry and Qualitative Analysis

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A chemist has to measure carefully, collect what a reaction gives off, and work out what an unknown substance contains. This chapter covers the apparatus and technique for measuring, collecting and drying gases and titrating, the tests that identify common ions and gases, and how to judge how good a measurement is.

Learning objectives

By the end of this chapter, you can:

Foundation O LEVEL

- choose apparatus to measure time, temperature, mass and volume
- choose a method to collect and dry a gas
- describe how to carry out a titration
- identify cations with aqueous sodium hydroxide and aqueous ammonia
- identify anions and gases with their tests

Core A LEVEL

- identify the A Level cations (Ba^{2+}, Cr^{3+}, Mg^{2+}, Mn^{2+}) and anions (Br^-, NO_2^-, SO_3^{2-})
- deduce an unknown substance from a sequence of observations
- explain why the order of tests and the choice of acid matter
- tell accuracy from precision
- find the largest source of error with percentage uncertainty

Prerequisites

Chapter 1 (filtration), Chapter 3 (ions), Chapter 4 (moles and concentration), Chapter 5 (acids, alkalis, amphoteric oxides, precipitation and titration) and Chapter 6 (oxidising and reducing agents). Fill in the blanks as the lesson goes.

7.1 Measuring physical quantities

Each measurement needs a quantity, an SI unit and apparatus that is accurate enough. The accuracy of an instrument is how closely it can read, for example ±0.01 g.

quantity	SI unit	apparatus and accuracy
time	second (s)	digital stopwatch ±0.01 s, analogue stopwatch ±0.1 s
temperature	kelvin (K)	alcohol, mercury or digital thermometer, temperature probe with data logger
length	metre (m)	metre rule ±0.1 cm, measuring tape ±0.1 cm to ±0.5 cm
mass	kilogram (kg)	electronic balance ±0.01 g
volume	cubic metre (m^3)	pipette, volumetric flask, measuring cylinder, burette, gas syringe

- Temperature in K = temperature in °C + _____.
- 1 dm^3 = _____ cm^3 = 1 litre. Although 1 m = 10 dm, 1 m^3 is 1000 dm^3, not 10.

7.1.1 Measuring volume

Choose the apparatus by the volume needed and the accuracy required.

apparatus	what it measures
pipette	one accurate fixed volume, such as 10.0 cm^3 or 25.0 cm^3
volumetric flask	one accurate fixed, larger volume, such as 100 cm^3 or 250 cm^3
measuring cylinder	a range of volumes to the nearest _____ cm^3
burette	a range of volumes to the nearest _____ cm^3
gas syringe	the volume of a gas, up to 100 cm^3

Read the volume with the eye level with the **meniscus**, the curved surface of the liquid. Reading from above or below gives a **parallax error** (Figure 7.1).

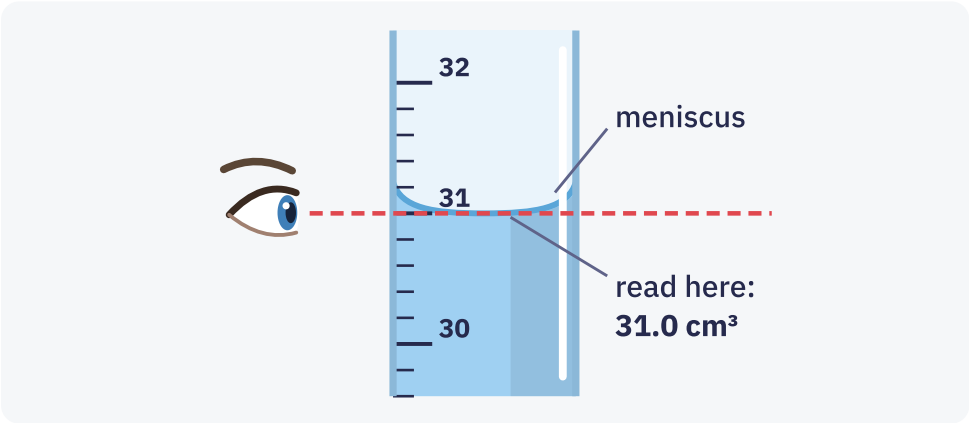


Figure 7.1 Read the bottom of the meniscus with the eye level with it.

Check your understanding

1. Give one advantage of a burette over a measuring cylinder.
2. Give one disadvantage of a pipette, even though it measures very accurately.

7.2 Collecting and drying gases

Choose how to collect a gas from two properties: its _____ in water and its _____ compared with air. A gas syringe collects small, accurate volumes. The three methods below collect larger volumes (Figure 7.2).

method	gas suited to it	example
water displacement	insoluble or slightly soluble in water, density does not matter	carbon dioxide
upward delivery	less dense than air, soluble or insoluble	ammonia
downward delivery	denser than air, soluble or insoluble	chlorine, hydrogen chloride, sulfur dioxide

In both air-displacement methods the gas pushes air out of the jar. A gas denser than air settles at the _____ of the jar, and a gas less dense than air collects at the _____.



Figure 7.2 Ways to collect a gas. Upward delivery suits a gas less dense than air, downward delivery a gas denser than air.

7.2.1 Drying gases

Pass the moist gas through a drying agent that does _____ with it. Chapter 5 tells you which ones react: an acidic drying agent reacts with a basic gas, and a basic drying agent reacts with an acidic gas.

drying agent	use it for	do not use it for
concentrated sulfuric acid (an acid)	most gases, including chlorine and hydrogen chloride	gases that react with it, such as ammonia, a base
quicklime, calcium oxide (a basic oxide)	ammonia	gases that react with it, such as carbon dioxide, an acidic oxide
calcium chloride	gases that do not react with it	ammonia

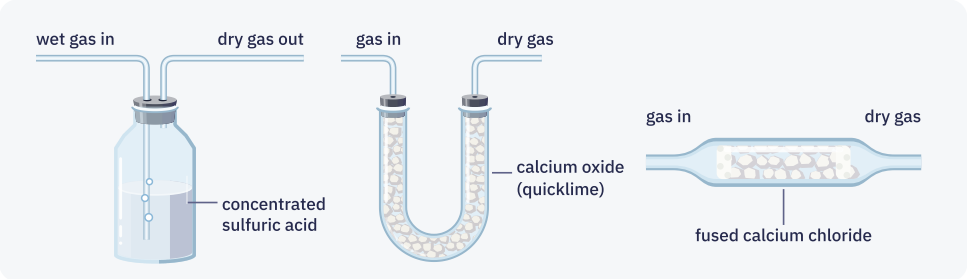


Figure 7.3 Three ways to dry a gas: bubbling it through concentrated sulfuric acid, or passing it over quicklime or fused calcium chloride.

NOTE Quicklime and calcium chloride absorb moisture from the air, so heat them just before use.

Check your understanding

1. Gas X is less dense than air and insoluble in water. Suggest a method to collect it.
2. Gas Y reacts with acids. Name one drying agent that can be used on it, and explain your choice.

7.3 Titration technique

Chapter 5 used titration results. This section is about getting them. The solution of known concentration, the **titrant**, goes in the burette. The solution being measured, the **analyte**, goes in the conical flask (Figure 7.4).

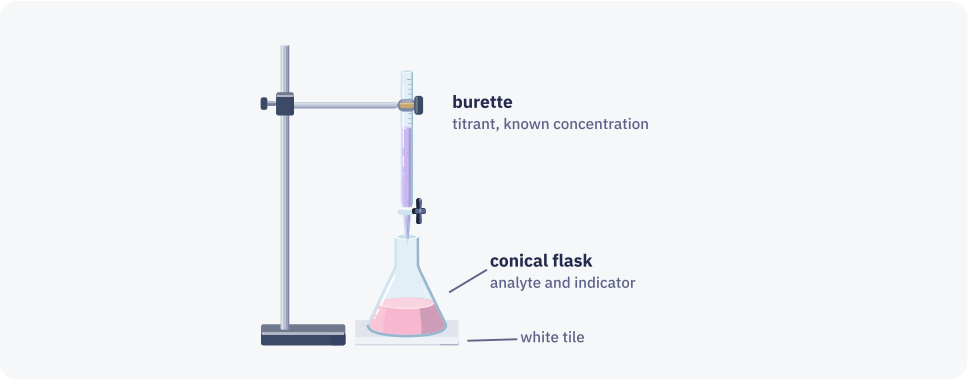


Figure 7.4 A titration: the titrant in the burette, the analyte and indicator in the flask on a white tile.

1 Measure out the analyte

- Use a pipette to put a fixed volume, usually 25.0 cm^3, into a clean conical flask.
- Add a few drops of indicator.

2 Run in the titrant

- Fill the burette and record the starting reading, with the eye level with the meniscus.
- Stand the flask on a **white tile**, so the colour change is easy to see.
- Add the titrant slowly, **swirling** the flask all the time. Near the end, add it drop by drop.
- Stop when the colour changes _____: the end-point. Record the final reading.

3 Work out and repeat

- Titre = final reading – starting reading. A burette reads to the nearest 0.05 cm^3, so record readings such as 23.45 cm^3.
- Repeat until two titres agree to within 0.10 cm^3, and use the average of those titres.

Check your understanding

1. Why is the conical flask swirled during a titration?

2. A burette reads 1.20 cm^3 at the start and 24.65 cm^3 at the end-point. What is the titre?

7.4 Testing for cations

Qualitative analysis finds out which ions or gases are present, not how much. Cations are identified with two alkalis, aqueous sodium hydroxide and aqueous ammonia. Add each a few drops at a time, then in excess. Most metal hydroxides are insoluble, so a metal cation gives a **precipitate** (ppt.) of its hydroxide (Chapter 5):

$$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s) \qquad Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$$

Three things identify the cation: the **colour** of the precipitate, whether it **dissolves in excess**, and whether **ammonia** is given off. The table follows the Qualitative Analysis Notes of the A Level Data Booklet. Mg^{2+}, Ba^{2+}, Cr^{3+} and Mn^{2+} are the A Level additions.

cation	with NaOH(aq)	with NH_3(aq)
aluminium, Al^{3+}	white ppt., _____ in excess	white ppt., insoluble in excess
ammonium, NH_4^+	ammonia given off on warming	–
barium, Ba^{2+}	no ppt.	no ppt.
calcium, Ca^{2+}	white ppt. only when $[Ca^{2+}]$ is high	no ppt.
chromium(III), Cr^{3+}	**grey-green** ppt., soluble in excess giving a dark green solution	grey-green ppt., insoluble in excess
copper(II), Cu^{2+}	**pale blue** ppt., insoluble in excess	blue ppt., soluble in excess giving a _____ solution
iron(II), Fe^{2+}	**green** ppt., turning brown in air, insoluble in excess	the same as with NaOH(aq)
iron(III), Fe^{3+}	**red-brown** ppt., insoluble in excess	the same as with NaOH(aq)
magnesium, Mg^{2+}	white ppt., insoluble in excess	white ppt., insoluble in excess
manganese(II), Mn^{2+}	**off-white** ppt., quickly turning brown in air, insoluble in excess	the same as with NaOH(aq)
zinc, Zn^{2+}	white ppt., soluble in excess	white ppt., _____ in excess

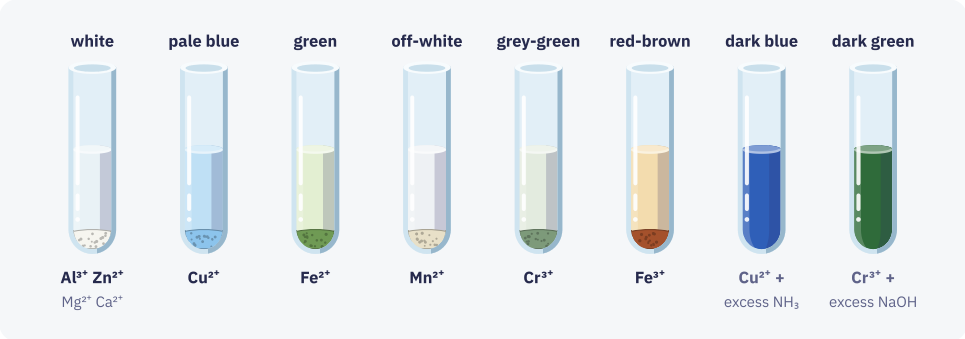


Figure 7.5 The colours seen in the cation tests.

Why the precipitates behave as they do:

- The hydroxides of zinc, aluminium and chromium(III) are **amphoteric**, like the oxides in Chapter 5. They react with excess sodium hydroxide to form soluble salts.
- Excess aqueous ammonia forms soluble compounds with copper(II) and zinc ions, so those two precipitates dissolve. Chapter 16 explains how.
- Iron(II) and manganese(II) hydroxides turn brown as air oxidises the metal to a higher oxidation state (Chapter 6).
- Na^+, K^+ and NH_4^+ give no precipitate because their hydroxides are soluble. Barium hydroxide is soluble too.

7.4.1 One test is often not enough

Several cations can give exactly the _____ in one test. A white precipitate with sodium hydroxide could be any of **four** ions (Al^{3+}, Zn^{2+}, Mg^{2+} or Ca^{2+}), and "no precipitate" could be NH_4^+ or Ba^{2+}. A single observation narrows the list. It does not name the ion. Follow each result to the end of its branch (Figures 7.5

and 7.6), and when more than one ion is still possible, do the other test and compare:

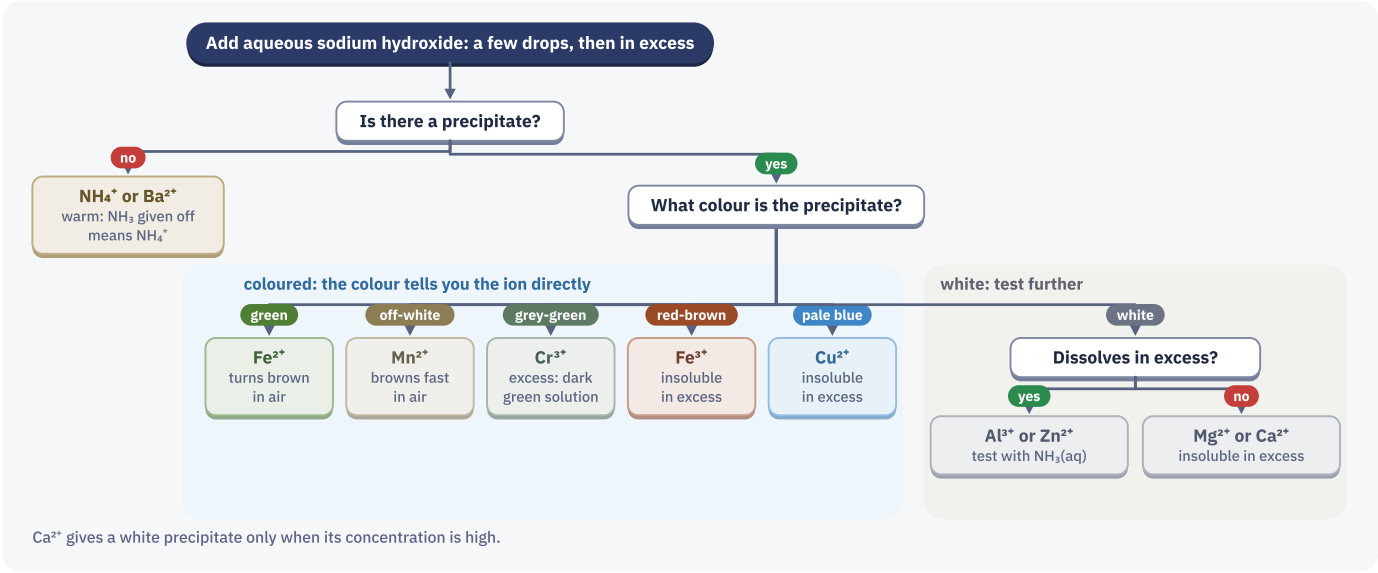


Figure 7.6 Identifying a cation with aqueous sodium hydroxide.

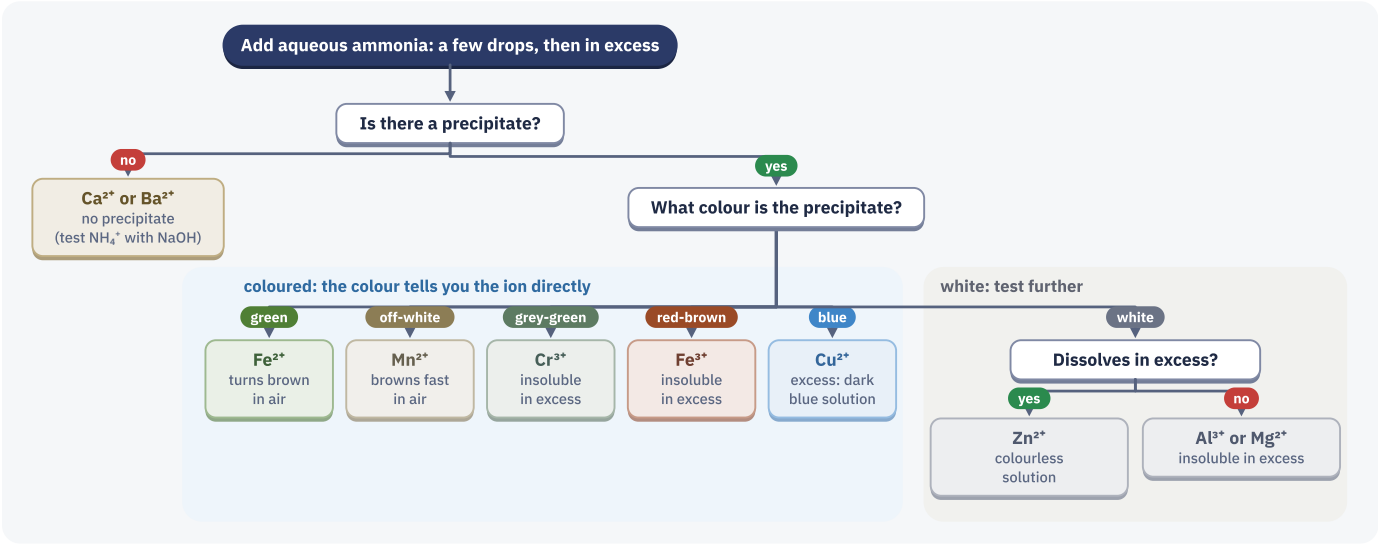


Figure 7.7 Identifying a cation with aqueous ammonia.

still possible after one test	do this	result
Al^{3+} or Zn^{2+} (dissolve in excess NaOH)	add excess NH_3(aq)	Zn^{2+} dissolves, Al^{3+} does not
Mg^{2+} or Ca^{2+} (insoluble in excess NaOH)	add NH_3(aq)	Mg^{2+} gives a white ppt., Ca^{2+} gives none
Al^{3+} or Mg^{2+} (insoluble in excess NH_3)	add excess NaOH(aq)	Al^{3+} dissolves, Mg^{2+} does not
NH_4^+ or Ba^{2+} (no ppt.)	warm with NaOH(aq)	NH_4^+ gives ammonia, Ba^{2+} gives none

Check your understanding

1. Compound X contains aluminium, calcium or zinc ions. Which reagent tells you which, and what would you see?
2. A solution gives a light blue precipitate with aqueous ammonia that dissolves in excess. What colour is the final solution, and which cation is present?
3. A solution gives a white precipitate with aqueous sodium hydroxide, insoluble in excess, and no precipitate with aqueous ammonia. Which cation is present?

7.5 Testing for anions

The anion tests also follow the Data Booklet. Bromide, nitrite and sulfite are the A Level additions.

anion	test	positive result
carbonate, CO_3^{2-}	add dilute acid	effervescence: CO_2 turns limewater milky
sulfite, SO_3^{2-}	add dilute acid	SO_2 given off: turns acidified $KMnO_4$ from purple to colourless. With $Ba^{2+}(aq)$ it gives a white ppt. that **dissolves** in dilute strong acid
nitrite, NO_2^-	add dilute acid	colourless NO given off, which turns (pale) **brown** in air as it forms NO_2
chloride, Cl^-	add dilute nitric acid, then aqueous silver nitrate	_____ ppt. of AgCl, soluble in $NH_3(aq)$
bromide, Br^-	add dilute nitric acid, then aqueous silver nitrate	pale **cream** ppt. of AgBr, partly soluble in $NH_3(aq)$
iodide, I^-	add dilute nitric acid, then aqueous silver nitrate	_____ ppt. of AgI, insoluble in $NH_3(aq)$
sulfate, SO_4^{2-}	add dilute nitric acid, then aqueous barium nitrate	white ppt. of $BaSO_4$, **insoluble** in excess dilute strong acid. Sulfite also gives a white ppt. with Ba^{2+} ($BaSO_3$), but it dissolves in the acid.
nitrate, NO_3^-	add aqueous sodium hydroxide, then aluminium foil, and warm	ammonia given off: turns damp red litmus blue

Each positive result is a reaction from an earlier chapter: an acid with a carbonate or sulfite, a precipitation ($Ag^+ + Cl^- \rightarrow AgCl$, $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$), or a redox reaction: aluminium reduces nitrogen from +5 in NO_3^- to −3 in NH_3, and sulfur dioxide reduces manganate(VII). Figure 7.8 puts the tests in order.

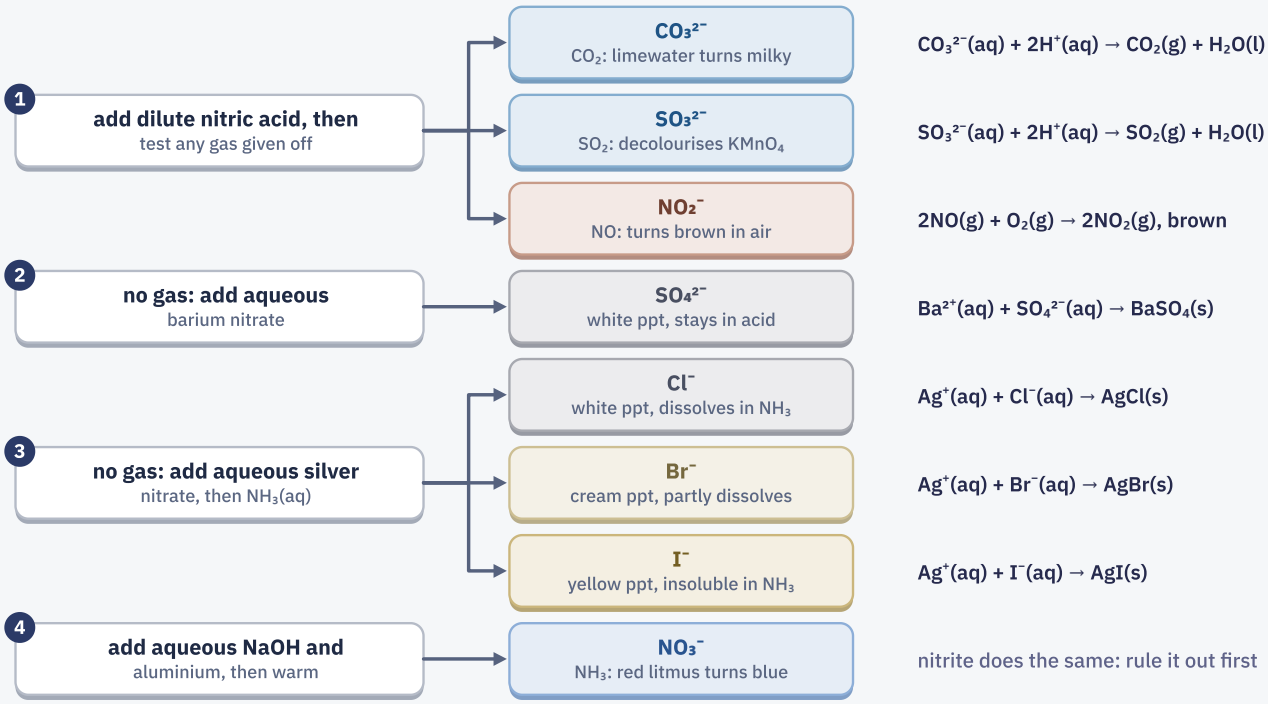


Figure 7.8 Identifying an anion.

EXAM TIP The order of the tests and the choice of acid change the result.

- Acidify with dilute **nitric** acid first. It removes carbonate, sulfite and hydroxide ions, which would also give precipitates with silver or barium ions.
- Never acidify with hydrochloric acid before a chloride test, or with sulfuric acid before a sulfate test: you would be adding the very ion you are testing for.
- Ammonium ions also give ammonia with warm sodium hydroxide. In the nitrate test, warm with sodium hydroxide alone first. Only ammonia that appears after adding aluminium shows nitrate. Nitrite gives ammonia this way too, so rule it out with dilute acid first.
- $BaSO_3$ and $BaSO_4$ are both white. Only $BaSO_3$ dissolves when dilute strong acid is added.

Check your understanding

1. Describe the test for sulfate ions in a solution.
2. A solution contains sodium chloride or sodium iodide. How would you tell which?
3. How would you tell a sulfite from a sulfate?

7.6 Testing for gases

gas	description	test	positive result
hydrogen, H_2	colourless, odourless	burning splint at the mouth of the tube	goes out with a 'pop'
oxygen, O_2	colourless, odourless	glowing splint into the tube	_____
carbon dioxide, CO_2	colourless, odourless	bubble through limewater	white precipitate, which dissolves on further bubbling
chlorine, Cl_2	pungent smell	damp blue litmus paper	turns red, then is _____
sulfur dioxide, SO_2	colourless, pungent smell	filter paper soaked in acidified $KMnO_4$	purple to colourless
ammonia, NH_3	colourless, pungent smell	damp red litmus paper	turns blue

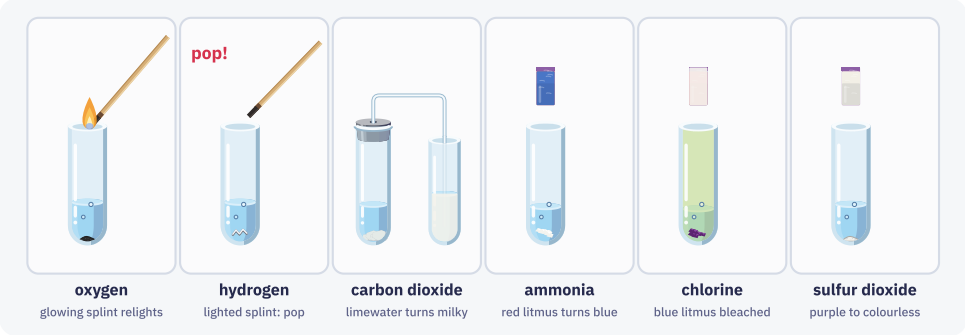


Figure 7.9 The six gas tests.

Again the tests use earlier chemistry. Ammonia is the only common alkaline gas (Chapter 5). Sulfur dioxide is a reducing agent (Chapter 6). Chlorine forms an acid with the water on the paper, then bleaches it.

WORKED EXAMPLE Solid K gives off a vapour on gentle heating that condenses to a liquid boiling at 100 °C. A solution of K gives a blue precipitate with aqueous sodium hydroxide, and on warming a gas turns damp red litmus blue. With aqueous ammonia the blue precipitate dissolves in excess. Acidified with dilute nitric acid, it gives a white precipitate with barium nitrate. What does K contain?

1. The liquid boiling at 100 °C is water. *K is hydrated: it has water of crystallisation.*
2. Blue precipitate dissolving in excess ammonia: Cu^{2+}. Ammonia gas on warming with NaOH: NH_4^+. *Two cations.*
3. White precipitate with barium nitrate after nitric acid: _____ *K is a hydrated copper(II) ammonium sulfate.*

Check your understanding

1. A reaction gives off a colourless, odourless gas. Which gases could it be, and how would you tell them apart?
2. Describe how to tell chlorine, ammonia and hydrogen apart.

7.7 Accuracy, precision and error

CORE · A LEVEL

Section 7.1 gave the accuracy of each instrument. Here we use those values to judge an experiment.

Accuracy is how close a result is to the _____. **Precision** is how close repeated measurements are to _____.

- Results can be precise but not accurate: tightly grouped, but all away from the true value (Figure 7.10).
- A better instrument or a correct reading improves _____. Repeating the measurement shows how good the _____ is.
- Reading the meniscus from above or below adds a parallax error to every reading.
- A **systematic error** affects every measurement in the same way, so repeating does not remove it. A **random error** makes results fluctuate around their mean, so averaging repeats reduces it.

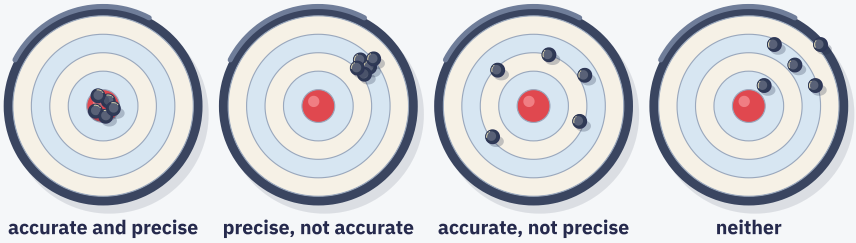


Figure 7.10 The centre of each target is the true value and each dot is one measurement. The dot positions are drawn for illustration.

To find the largest source of error, compare the percentage uncertainty of each measurement.

$$\text{percentage uncertainty} = \frac{\text{uncertainty of the instrument}}{\text{measured value}} \times 100\%$$

WORKED EXAMPLE An experiment uses 5.0 cm^3 of acid measured in a measuring cylinder (±0.5 cm^3) and 2.00 g of solid weighed on an electronic balance (±0.01 g). Which measurement is the larger source of error? What change reduces it?

1. Cylinder: 0.5 ÷ 5.0 × 100% = 10%	*Uncertainty divided by the reading.*
2. Balance: 0.01 ÷ 2.00 × 100% = 0.5%	*The same calculation for the balance.*
3. The cylinder is the larger source of error.	*10% is much greater than 0.5%.*
4. Use a burette (±0.05 cm^3): 0.05 ÷ 5.0 × 100% = _____	*A smaller instrument uncertainty gives a smaller percentage.*

Check your understanding

1. Which has the larger percentage uncertainty: 20.0 cm^3 in a measuring cylinder (±0.5 cm^3) or 2.00 g on a balance (±0.01 g)?
2. Five readings of one mass are 5.21 g, 5.20 g, 5.22 g, 5.21 g and 5.20 g. The true mass is 5.00 g. Are the readings accurate, precise, both or neither?

Answers to Check your understanding

7.1

1. A burette is more accurate (nearest 0.05 cm^3 against 0.5 cm^3) and can measure a range of volumes.
2. A pipette measures only one fixed volume.

7.2

1. Water displacement, because the gas is insoluble. Upward delivery also works, because the gas is less dense than air.
2. Quicklime (calcium oxide). A gas that reacts with acids is basic or reacts like a base, so concentrated sulfuric acid would react with it.

7.3

1. To mix the titrant with the analyte, so the colour change appears exactly when enough has been added.
2. 24.65 – 1.20 = 23.45 cm^3

7.4

1. Aqueous sodium hydroxide, then aqueous ammonia. A white precipitate insoluble in excess sodium hydroxide shows calcium. If it dissolves in excess sodium hydroxide, add aqueous ammonia: insoluble in excess shows aluminium, soluble in excess shows zinc.
2. Dark blue. Copper(II) ions.
3. Calcium, Ca^{2+}. Mg^{2+} would also give a white precipitate with aqueous ammonia.

7.5

1. Add dilute nitric acid, then aqueous barium nitrate. A white precipitate of barium sulfate shows sulfate ions.
2. Add dilute nitric acid, then aqueous silver nitrate. A white precipitate shows chloride. A yellow precipitate shows iodide.
3. Add dilute acid: a sulfite gives sulfur dioxide, which turns acidified $KMnO_4$ colourless, and a sulfate gives no gas. (With Ba^{2+}, only the sulfite precipitate dissolves in dilute acid.)

7.6

1. Hydrogen, oxygen or carbon dioxide. A burning splint goes out with a pop in hydrogen, a glowing splint relights in oxygen, and carbon dioxide turns limewater milky.
2. Damp red litmus turns blue in ammonia. Damp blue litmus turns red and is bleached by chlorine. A burning splint goes out with a pop in hydrogen.

7.7

1. The cylinder: 0.5 ÷ 20.0 × 100% = 2.5%, against 0.01 ÷ 2.00 × 100% = 0.5% for the balance.
2. Precise but not accurate. The readings agree closely with each other but are all about 0.2 g above the true mass.