

Advanced Level Practical Guide

SAFETY AND LABORATORY RULES

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Accidents in a chemical laboratory usually result from improper judgment on the part of the victim or one of his/her neighbors. Learn and observe the safety and laboratory rules listed below.

1. Notify your instructor at once in case of any accident or personal injury to you or your neighbor, even if apparently minor.

If your instructor is temporarily absent, notify the instructor in the adjoining lab, or one of the stockroom personnel. If you are asked to go see the nurse, you must go. Refusal to do so is grounds for being dropped from the course.

2. Wear safety goggles. Because the eyes may be permanently damaged by spilled chemicals and flying broken equipment, be sure to wear safety goggles or safety glasses (State law) whenever anyone is working in the lab. The laboratories are equipped with eye wash fountains. Learn their location and how to use them the first day in the lab.

If you get anything in your eye, use the eye wash immediately, and then report it to your instructor. Use your hands to hold your eye open so that it can be rinsed thoroughly.

Note: Eye washing with a *contact lens* in place will not clear a splashed chemical from the eye. The contact must be removed for effective cleansing. It is advisable for those wearing contacts to switch to glasses for the lab period.

3. Locate safety equipment. During the first laboratory period familiarize yourself with the location and operation of the safety features of the laboratory, including:

- Safety shower

Use-- if your clothing catches on fire or a corrosive chemical is spilled on you in quantities that cannot be easily flushed away at laboratory faucets.

- Eye wash
- Fire extinguishers
- Fire blanket
- Laboratory first aid kits
- Spill cleanup kits

A diagram of the lab is included.

4. Know the ways to put out a fire.

a) If it is open fire, such as a large chemical spill on a lab bench, the correct extinguisher should be used as follows:

- Pull the pin.
- Point the extinguisher (of dry) or hose (if CO₂) at the base of the fire.
- Squeeze the handle while moving the extinguisher back and forth.

NOTE: *Be careful not to spread the fire by getting the nozzle of the extinguisher too close--*

the material being emitted is under pressure.

b) If it is a small, contained fire, such as in a flask or beaker, cover the container with a piece of ceramic, cutting off the supply of oxygen to the fire and thus putting it out.

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5. Be careful when using glassware. Cuts and burns are the most common injuries that occur in chemistry laboratories. Cuts can be prevented by following a few simple rules:

a) When inserting glass tubing into rubber stoppers, use the following procedure:

- 1) Make sure the glass tubing ends are fire polished.
- 2) Always use glycerin or soapy water as a lubricant both on the tubing and in the hole.
- 3) Protect your hand by wrapping the glass tubing with a towel.
- 4) Hold the glass near the end to be inserted, thus minimizing the torque, and insert using a twisting motion. Never hold the glass at a bend.

b) Fire polish all sharp edges of broken glass.

c) Discard cracked or broken glassware in the designated container.

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d) Never heat heavy glassware such as graduated cylinders, suction flasks, or reagent bottles since they might shatter.

6. Wash chemicals from skin.

a) If you receive a chemical burn from a caustic material, i.e. acid or base, immediately wash the burned area with large quantities of water. Ask another student to summon the lab instructor.

b) Wash your hands and face quickly and thoroughly whenever they come into contact with a chemical.

c) Always wash your hands, before leaving the lab since toxic chemicals may be transferred to the mouth at a later time.

d) Chemicals spilled over a large part of the body require immediate action. Remove all contaminated clothing and use the safety shower, flooding the burned area. Do not use salves, creams, lotions, etc. Get medical attention.

7. Be careful with flames. A lighted gas burner can be a major fire hazard.

a) General Precautions:

1) The burner should be burning only for the period of time in which it is actually utilized.

2) Before lighting your burner carefully position it on the desk away from flammable materials, overhanging reagent shelves, flammable reagents such as acetone, toluene, and alcohol on neighboring desks.

3) Be careful not to extend your arm over a burner while reaching for something.

b) Personal Precautions:

1) Keep long hair tied back so that it cannot fall forward into a flame.

2) Keep beards away from flames.

8. Never point a test tube toward a laboratory neighbor or yourself when:

a) Heating a test tube over a burner.

b) Carrying out a reaction in a test tube.

9. Wear suitable clothing. Wear clothing that will protect you against spilled chemicals or flaming liquids. Hard-soled, covered footwear must be worn in the laboratory at all times--**no sandals**

allowed.

10. Assume that a particular reagent is hazardous unless you know for sure it is not.

a) Never taste a chemical unless specifically directed to do so.

b) If you are instructed to smell a chemical, point the vessel away from your face and carefully

fan the vapors toward your face with your hand and sniff gently.

c) Material Safety Data Sheets are available.

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11. Never fill a pipet by using your mouth.

12. Assemble safe apparatus. Always assemble an apparatus as outlined in your instructions.

Makeshift equipment and poor apparatus assemblies are the first steps to an accident.

13. Dilute concentrated acids and bases by pouring the reagent into water (room temperature or

lower) while stirring constantly. Never pour water into concentrated acids; the heat of solution

will cause the water to boil and the acid to splatter.

To help you remember--"*Do as you oughter, pour acid into water.*"

14. Use the fume hoods. Any experiment involving the use of or production of poisonous or irritating gases must be performed in a hood.

15. Read the label. Read the label carefully, *read it twice*, before taking anything from a bottle. Many

chemicals have similar names, such as sodium sulfate and sodium sulfite. Using the wrong reagent can spoil an experiment or can cause a serious accident.

16. Eating, drinking, and smoking are strictly prohibited in the laboratory at all times because of the

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possibility of chemicals getting into the mouth or lungs through contamination. The chief hazard with smoking is fire.

17. Avoid rubbing your eyes unless you *know* your hands are clean.

18. Do not put hot objects on the desktops. Place hot objects on a wire gauze or ceramic pad.

19. Never throw lighted matches into a sink. They may ignite a discarded flammable liquid.

20. Perform only authorized experiments. Unless authorized to do so by the instructor, a student will be subject to immediate and permanent expulsion from the lab if:

- a) Attempting to conduct unauthorized experiments.
- b) Attempting variations of the experiment in the lab manual

Performing unauthorized experiments are dangerous. Students lack the experience to recognize whether or not the chemicals and techniques are safe.

21. Keep your workspace orderly.

- a) Place tall items, such as graduated cylinders, toward the back of the workbench so they will not be overturned by reaching over them.
- b) Clean up all chemical spills, scraps of paper, and glassware immediately.
- c) Keep drawers closed while working and the aisles free of any obstructions, including chairs.
- d) Never place coats, books, and other belongings on the laboratory bench where they will interfere with the experiment and are likely to be damaged.

22. Clean up your workspace at the end of each laboratory period.

- a) Wash and wipe off your desktop.
- b) Be sure gas and water are turned off.
- c) Return all special equipment to the stockroom.
- d) Put everything back into your locker drawer and lock.

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23. Avoid using excessive amounts of reagent.

- a) Never use more than called for in the experiment.
- b) Do not return any excess chemical to the reagent bottle; share it with another student or dispose of it according to the instructions listed in #24.
- c) If you are uncertain how to dispose of an excess of a specific chemical, consult your instructor.

24. Discard waste chemicals as follows:

Waste Chemical Proper Disposal

- a) Non-flammable water-soluble liquids Liquid Waste bottle
- b) Chemical solids, contaminated paper, and Solid Waste bottle
- c) Paper products Trash can
- d) Organic solvents Organic Waste bottle

(Do not put acids in the organic waste bottle.)

- e) Glass tubing waste or broken glass Broken Glass wooden box

25. Always add a reagent slowly--never "dump" in. Two reasons:

- a) Some reactions give off a lot of heat, and unless adding slowly, can become too vigorous and out of control.
- b) If you make a mistake and choose the wrong chemical, adding slowly decreases the possibility of causing a serious accident.

26. Treat chemical spills as follows:

- a) Alert your lab neighbors and your instructor.
- b) Clean up the spill as directed by your lab instructor.

27. Never fill a vessel more than about 70% capacity if you plan to heat it, unless specifically told to do so.

28. Never work in the lab without the instructor present. This includes setting up equipment.

29. Maintain a wholesome, businesslike attitude in the lab. Horseplay and other acts of carelessness are prohibited.

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30. Be aware of your lab neighbors' activities; you may be a victim of their mistakes.

If you observe

improper techniques or unsafe practices:

a) Advise your neighbor.

b) Advise your instructor if necessary.

31. Observe all specific precautions and modifications mentioned in each experiment.

32. Do not remove any chemicals from the lab.

33. For reasons of safety, you may not be allowed to attend lab if you are late.

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UNIT ONE

PRELIMINARY TESTS FOR ANIONS

The Appearance of Substances

It is always advisable to note the physical properties of a substance. This is an important test to do whether or not one is asked because from it, a clue about the substance may be formulated. Thus physical properties like appearance colour, smell or solubility in water could lead to use inferences as described below and hence one is guided as to the possible identity of the substance.

I. COLOUR

- If a compound and its aqueous solution are colourless, it probably means absence of transition metal ion.
- If the substance is a black solid, presence of an oxide or a sulphide could be inferred.
- If the substance is a solid, and/or its aqueous solution is coloured, probably a transition metal ion is present. (See texts on theoretical chemistry for explanation). The following are some typical characteristic colours of some cations.

Cation	Colour
Mn(VII) as in MnO_4^-	Very dark purple
Mn(VI)	Dark blue – green
Mn(II)	Very pale pink, not visible in solution
Fe(II)	Pale blue-green
Fe(III)	Golden yellow or brown in solution
Ni(II)	Green
Cu(II) or Cu(I)	Blue, blue – green or green
Cr(III)	Blue-green, green or pale violet
Cr(VI) as in $\text{Cr}_2\text{O}_7^{2-}$	Yellow or orange

II. SMELLS

Usually on heating a sample of an unknown substance or occasionally even at room temperature, the following smells may be detected.

Observation	Inference
Smell of ammonia	Ammonium salt

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Smell of SO₂

Sulphite

Smell of H₂S

Sulphide

III. SOLUBILITY IN WATER

When a solid does not dissolve in water, it is generally right to infer the presence of such compounds like CO_3^{2-} , SO_4^{2-} , OH^- or O^{2-} other than on Group I metals; Cl^- , I^- or Br^- of lead or AgCl etc.

IV. THE ACTION OF HEAT

Certain compounds are thermally unstable and will therefore decompose on heating. The experimental procedure is to heat a little (say one micro-spatula end –full) of the unknown solid in a dry and hard-glass or Pyrex test –tube (an ignition tube is always best); first gently and then more strongly afterwards until no further change occurs.

In the majority of cases, a gas is evolved during the heating, which includes water vapour. If a gas is evolved, it must be carefully and properly identified by its smell, colour, action on moist litmus paper, action on lime-water, action on splint and the usual confirmatory test (see under Tests for Gases).

Always make sure to observe the residue as well since useful information may be obtained from it. Evidence may be obtained from:-

a) Gas evolved	Inference
(i) NH ₃	from NH_4^+ salt
(ii) HCl	from hydrated Cl^- (excluding Group I chlorides or BaCl ₂)
(iii) Br ₂ / I ₂	from Br^- or I^-
(iv) SO ₂ and/or H ₂ S	from various sulphur compounds e.g HSO_3^- , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$ and even certain SO_4^{2-} or hydrated S^{-2}
(v) SO ₃	from SO_4^{2-} (not of Group I, Ca ²⁺ or Ba ²⁺)
(vi) NO ₂ and O ₂	from NO_3^- s other than Group I or NH_4^+
(vii) O ₂	from NO_3^- s of Group I and from other oxygen-rich compounds like chlorates, peroxides or manganate (VII) or higher oxides.

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- (viii) CO_2 from HCO_3^- s, CO_3^{2-} s and some oxalates
(but excluding Group I) and barium carbonates.
- (ix) Water vapour from hydrated salts or hydroxides
- (x) CH_3COCH_3 from ethanoates (the vapour has sweet smell and burns)

b) **Sublimate**

This may be the original substance, implying covalent character, or an ammonium salt (white sublimate). A yellow sublimate which melts easily infers sulphur.

c) **Residue**

In many cases this is an oxide of the metal ion present. The following are typical examples:-

Observation	Inference
(i) Yellow (hot), white (cold)	Zinc oxide (ZnO)
(ii) Brownish (hot) yellow Or yellowish brown (cold)	Lead (II) oxide (PbO)
(iii) Black (hot), reddish brown (cold)	Iron (III) oxide (Fe_2O_3)
(iv) Black	Copper (II) oxide
(v) "Charring" or uneven blackening	Presence of carbon
(vi) Dark brown	Lead (IV) oxide (PbO_2)

V. TESTS FOR GASSES

When a gas is evolved during an experiment, it MUST be tested so that it can be identified completely. It is wise to OBSERVE, SMELL and finally TEST THE GAS CHEMICALLY. This is because the human organs of sight and smell are much more sensitive than simple chemical tests. So use your YES and NOSE first and foremost.

When using chemical reagents like lime-water, solutions of silver nitrate or of potassium manganate (VII) for testing gases, remember to take small quantities of reagents because they are thus more sensitive.

Tests in which a solution changes colour, for example KMnO_4 (aq) from purple to colourless or $\text{K}_2\text{Cr}_2\text{O}_7$ (aq) from orange to green (test for SO_2) or KI (aq) from colourless to dark-brown (test for Cl_2) are best done using a small strip of "filter" paper whose tip has been dipped in the test reagent.

The following properties may be used to identify the gases specified.

Gas	Appearance or colour	Smell	Effect on litmus	Confirmatory Tests
Br_2	Deep brown (red), Turns to liquid	*pungent	Bleaches	Forms a brown Solution in a drop of tetra chloromethane

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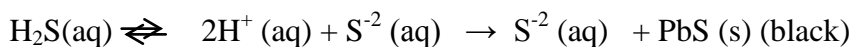
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2. The gas neutralizes ammonia to give NH_4Cl (g)

H_2S Colourless *like rotten eggs weakly acidic darkens a solution containing Pb^{2+} ions

Explanation: Hydrogen sulphide dissociates in solution as follows:

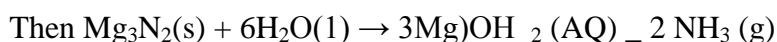
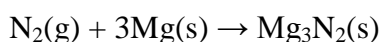


I_2 purple vapour, *Pungent Bleaches Gives blue colour with starch solution and gives
Black solid slowly purple colour in CCl_4 (see Br_2)

Explanation: The blue colour formed with starch is due to the adsorption of iodine onto the starch molecules forming starch-iodine complex. The purple colour is a solution of iodine in CCl_4 .

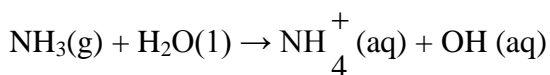
N_2 Colourless odourless neutral Very un reactive, Mg burns init to
give white ash (Mg_3N_2), which dissolves in cold H_2O giving off NH_3 gas.

Explanation: Nitrogen is very reactive gas due to the stability of the $\text{N} \equiv \text{N}$ triple bond. But the bond can be broken by very high energy like from the flame of burning magnesium:-



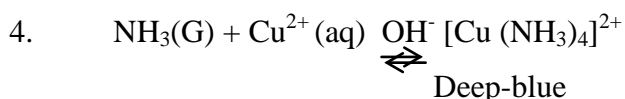
NH_3 colourless Pungent alkaline Dense white fumes
*smell of goat's urine with conc. HCl and turns
 $\text{CuSO}_4(\text{aq})$ more intensely blue.

Explanation 1: Is alkaline because it dissociates in water yielding OH^- ions thus



2. Forms NH_4Cl when reacted with the acidic HCl (see under HCl above)

3. Complexes with copper (II) to form $[\text{Cu}(\text{NH}_3)_4]^{2+}$, which is deep-blue in colour.



N_2O Colourless Sweetish Neutral Rekindles a glowing splint

Explanation: Nitrogen (IV) oxide is very readily decomposed by heat. Besides, it is an endothermic compound. Thus the oxygen produced on decomposition supports combustion.

NO Colourless but smell of * NO_2 Neutral though
Turns to brown (NO_2) NO_2 is acidic

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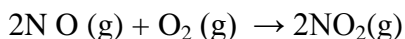
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When exposed
To air

Darkens FeSO₄
Solution

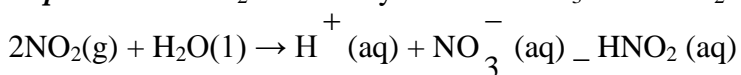
Explanation 1: Readily oxidized to nitrogen (IV) oxide, which is brown.



2. The brown with iron (II) sulphate is due to nitrosyl iron (II) complex Fe (NO_ 5H₂O (see brown ring test)

NO ₂	brown	*strong and unpleasant	acidic	darkens FeSO ₄ solution; does not form a liquid or bleach litmus.
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Explanation: NO₂ is the anhydride of HNO₃ and HNO₂.



PH ₃	Colourless	*like rotten fish	Neutral	Very inflammable, sometimes burns without ignition, giving white fumes.
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Explanation:

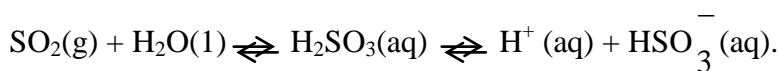
The spontaneous ignition is probably due to P₂H₄ and the white fumes are P₄O₁₀ 4PH₃ (g) + 8O₂(g) → P₄O₁₀ (g) + 6H₂O(l)

O ₂	Colourless	Odourless	Neutral	Rekindles a glowing splint
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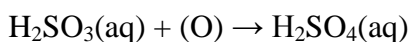
Explanation: Combustion is faster in pure oxygen compared to ordinary air.

SO ₂	colourless	*sharp and choking smell of burning sulphur	Decolourises KMnO ₄ (aq) Turns Cr ₂ O ₇ ²⁻ (aq) green
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Explanation: Acidity is due to formation of H₂SO₃



Sulphurous acid is readily oxidized to sulphuric acid while Mn (VII) and Cr (VI) are reduced to Mn (II) and Cr (III) respectively.

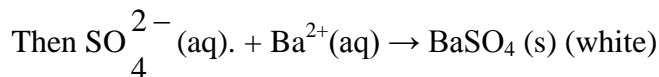
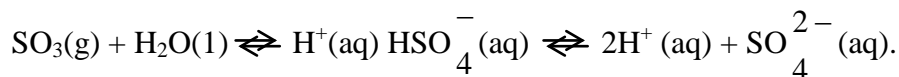


SO ₃	Smoky white fumes	*chiking	Acidic	Turns BaCl ₂ or solution on glass rod milky.
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Explanation: This is the acid anhydride of sulphuric acid



H_2O (II) (water vapour)	colourless	odourless	neutral	turns anhydrous copper sulphate blue, turns cobalt
	Condenses into			
	Colourless liquid			(II) chloride paper pink

Explanation: Water vapour hydrates copper (II) sulphate and cobalt (II) chloride.

NOTE: Asterisk (*) indicates

*Poisonous gases: MUST BE SMELT WITH CARE

VI. ACTION OF ACIDS

a) Dilute Hydrochloric Acid

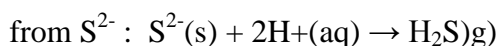
Dilute hydrochloric acid is a strong acid. It therefore liberates various acids from the anions of their salts. In two cases a volatile free acid is liberated, viz: (H_2S and CH_3COOH). In the other cases the free acid so liberated readily decomposes. Thus when dilute hydrochloric acid is added to a substance the following can be observed.

Evolution of hydrogen chloride means nothing but the following may be observed.

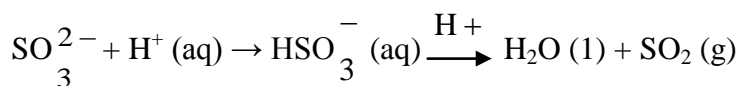
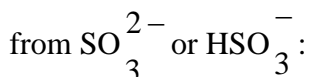
Observation

Inference

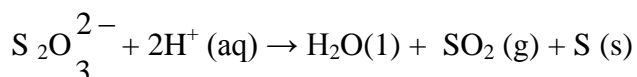
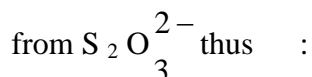
H_2S evolved



SO_2

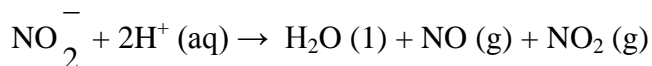


SO_2



The sulphur appears milky or yellowish

NO and NO_2 from NO_2^- . A blue solution maybe present



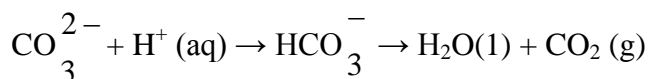
The blue solution is due to N_2O_3

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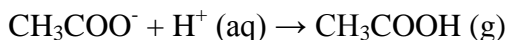
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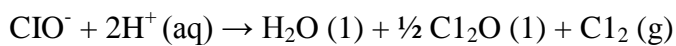
CO₂ from CO₃²⁻ or HCO₃⁻; generally with effervescence



CH₃COOH from ethanoates; Ethanoic acid has a faint sharp smell.



Cl₂ from hypochlorite, or from a strong oxidizing agent acting on the hydrochloric acid. If the test is positive, repeat using dilute nitric acid. If Cl₂ is again evolved, the unknown is a hypochlorite.



(from a strong oxidizing agent)

b) Concentrated Sulphuric Acid

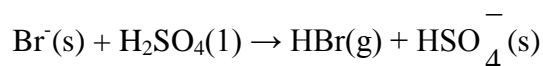
Sulphuric acid is a very strong acid. As such it will add protons readily to the anions of almost all other acids thus displacing the corresponding acids from their salts. It is also a strong oxidizing and dehydrating agent. So in some cases the free acid is liberated. Examples of the free acids liberated are hydrochloric and nitric acids. In other cases the acid is dehydrated. Examples of acids dehydrated by sulphuric acid are methanoic acid (HCOOH), ethanedioic acid, (COOH)₂ or C₂H₂O₄ and chromic acid H₂CrO₄. In yet other cases oxidation occurs e.g HBr and HI. During the actual experiment a little concentrated sulphuric acid is added to some of the unknown solid. The mixture is warmed, if necessary, but **NOT BOIL** the evolution of sulphur dioxide or sulphur trioxide indicates nothing. Otherwise the following may be observed:-

Observation	Inference
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HC1 Evolved	from chloride:
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HBr + Br ₂ evolved	from bromide
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Some HBr is oxidized to Br₂ according to the equation $2\text{Br}^- (\text{aq}) \rightarrow \text{Br}_2(\text{aq}) + 2\text{e}^-$

I ₂ + H ₂ S	from iodide: $\text{I}^- (\text{s}) + \text{H}^+(\text{l}) \rightarrow \text{HI}(\text{g})$
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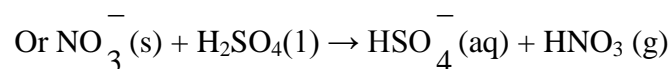
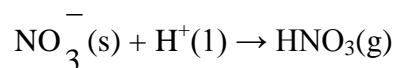
Some HI is oxidized I₂ in a similar way to HBr. Iodine appears as a purple vapour and a brownish solid. The hydrogen iodide or hydriodic acid evolved is a powerful reducing agent. It reduces sulphuric acid largely to hydrogen sulphide and is itself oxidized to hydrogen.

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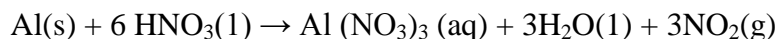
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 HNO_3

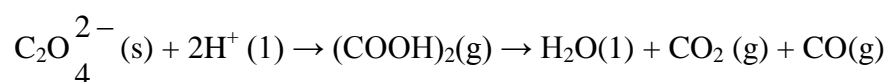
from a nitrate:



The nitric acid appears as very pale brown steamy fumes. If a little of Devarda's alloy, or copper turning is added, brown fumes of nitrogen (IV) oxide confirms a nitrate present. Devarda's alloy is a Al/Zn/Cu alloy. The alloy or copper reduces nitric acid as shown below.

 $\text{CO}_2 + \text{CO}$

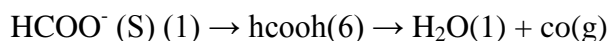
from ethanedioate:



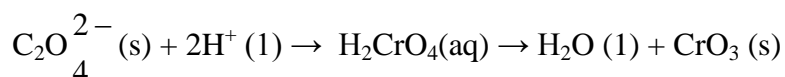
Test for CO_2 first because the burning of CO produces CO_2

CO

From mechanoate:



There maybe slight effervescence

 CrO_3 from CrO_4^{2-} :

Chromium (VI) oxide is a dark red solid.

So the actions of heat dilute hydrochloric acid and of concentrated sulphuric acid surveyed above may serve as **PRELIMINARY** tests for **ANIONS**. But the tests described below are further tests, some or all of which may be used as **CONFIRMATORY TESTS** for the appropriate anion.

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UNIT TWO

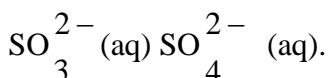
FURTHER (CONFIRMATORY) TESTS FOR ANIONS

a) **Sulphide ion, S^{2-} :**

1. Mix the solid with an excess of manganese (IV) oxide and heat. Evolution of sulphur dioxide shows the presence of sulphide ion except sulphides of Group I metals $S^{2-}(s) + 3(O) \rightarrow O^{2-}(s) + SO_2(g)$.
2. If the unknown is soluble in water, test the aqueous solution with a solution containing lead (II) ions e.g. aqueous lead (II) nitrate or lead (II) ethanoate solution. Formation of a black precipitate of lead (II) sulphide confirms presence of sulphide ion. $S^{2-}(aq) + Pb^{2+}(aq) \rightarrow PbS(s)$
(black)
3. Mix the unknown solid with Devarda's alloy. Add dilute hydrochloric acid to the mixture and warm the mixture. If hydrogen sulphide is evolved, the presence of the sulphide ion is confirmed. (The test is most appropriate for insoluble sulphides).

b) **Trioxosulphur (IV) (Sulphite): SO_3^{2-}**

1. The anion is a reducing agent. It may be oxidized using oxidizing agents like hydrogen peroxide, halogens or iodates. After oxidation, the solution of sulphite contains the sulphate ion, which may be tested (see under SO_4^{2-} ion).

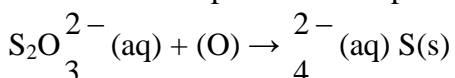


2. To a solution of the unknown add aqueous silver nitrate drop-wise until in excess. A white precipitate of Ag_2SO_3 readily soluble in excess silver nitrate confirms sulphite. $SO_3^{2-}(aq) + 2Ag^+(aq) \rightarrow Ag_2SO_3(s)$

The silver sulphite is very soluble in excess silver nitrate solution due to formation of complex ions like $[AgSO_3]$ OR $[Ag(SO_3)_2]^{2-}$

c) **Trioxosulphur (II) (Thiosulphate) ion; $S_2O_3^{2-}$**

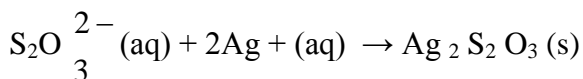
1. This is another reducing agent. When aqueous solution of potassium manganate (VII) acidified with aqueous sulphuric acid is added to the solution of the unknown a pale yellow or white suspension of sulphur is formed.



2. To an aqueous solution $S_2O_3^{2-}$, add aqueous solution of silver nitrate. A white precipitate of $Ag_2S_2O_3$ confirms thiosulphate ions.

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The precipitate turns brown because silver thiosulphate rapidly tends to decompose into silver sulphide. It also dissolves in excess silver nitrate due to formation of complex ions like $[\text{AgS}_2\text{O}_3]^-$ and $[\text{Ag}(\text{S}_2\text{O}_2)_2]^{3-}$.

3. To an aqueous solution of a $\text{S}_2\text{O}_3^{2-}$, add aqueous solution of lead (II) ethanoate.

Formation of a white precipitate of PbS_2O_3 soluble in excess reagent confirms presence of $\text{S}_2\text{O}_3^{2-}$. $\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{Pb}^{2+}(\text{aq}) \rightarrow \text{PbS}_2\text{O}_3(\text{s})$.

The precipitate forms complex ion, $\text{PbS}_2\text{O}_3^{2-}$, which is soluble in excess lead (II) ethanoate.

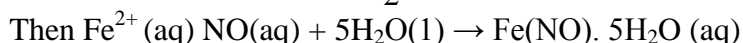
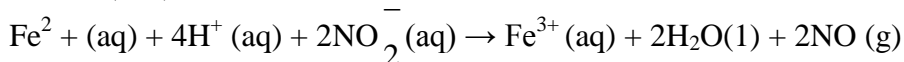
The precipitate turns grey on boiling because lead (II) thiosulphate decomposes to lead (II) sulphide on heating.



d) Nitrite, NO_2^- ion:

1. This is another reducing agent. After oxidation the solution contains nitrate ions. Oxidizing agents include aqueous MnO_4^- hydrogen peroxide or $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$. $\text{NO}_2^-(\text{aq}) + (\text{O}) \rightarrow \text{NO}_3^-(\text{aq})$

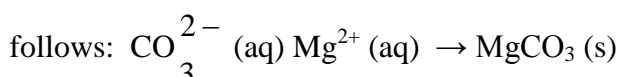
2. To a solution of a nitrite, add freshly prepared aqueous iron (II) sulphate followed by dilute ethanoic acid. Formation of a brown solution of the penta aquo nitrosyl iron (II) complex ion, $\text{Fe}(\text{NO}) \cdot 5\text{H}_2\text{O}$ confirms a nitrite ion.



e) Carbonate, CO_3^{2-} ion

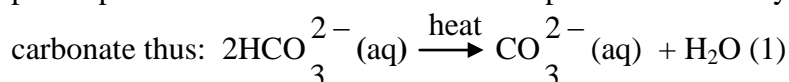
1. Most carbonates are insoluble in water. Hence an insoluble solid which gives carbon dioxide with effervescence on addition of dilute hydrochloric acid certainly implies presence of a carbonate ion.

2. If a carbonate is soluble, add a few drops of phenolphthalein solution. If a pink colouration appears it implies presence of CO_3^{2-} because carbonates are hydrolyzed readily in water as follows:



f) Hydrogen Carbonate, HCO_3^- ION:

1. An aqueous solution of a hydrogen carbonate is almost neutral. On boiling a hydrogen carbonate solution, carbon dioxide is evolved and the resultant solution is alkaline to phenolphthalein. This is due to decomposition of the hydrogen carbonate to a normal carbonate thus:

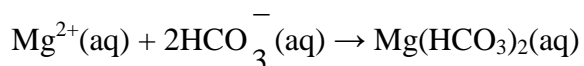


2. Add aqueous magnesium sulphate to a solution of a hydrogen carbonate and boil. If a white precipitate forms on boiling, a hydrogen carbonate ion is confirmed.

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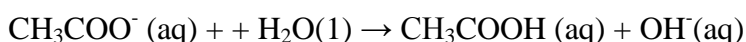
It should be noted that all other hydrogen carbonates except those of Group I metal ions are liquids or non-existent because they are highly unstable.

g) Ethanoate, $\text{CH}_3\text{COO}^{-}$ ion:

1. To a sample of the unknown, add about 2 cm³ of ethanol followed by 2 – 3 drops of concentrated sulphuric acid. Warm the mixture. If a sweet smelling liquid (ethylethanoate) is produced, the presence of the ethanoate ion is confirmed.



2. To an aqueous solution of the ethanoate, add 1 – 2 drops of iron (III) chloride in neutral solution. A red colouration infers ethanoate ion. Being the anion of a weak acid, the ethanoate ion is hydrolyzed, though slightly in solution according to the equation.



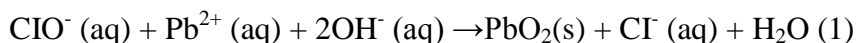
It is the iron (III) hydroxide, which forms as a colloidal solution which accounts for the red colouration.

h) Oxo chloride (Hypochlorite), ClO^{-}

1. Add cobalt (II) nitrate solution to a solution of the unknown. If a black precipitate of cobalt (II) (III) oxide forms accompanied by evolution of oxygen gas, the presence of oxo chloride ion is confirmed. Oxygen is formed because cobalt (II) oxide catalyses decomposition of the anion according to the following equation.

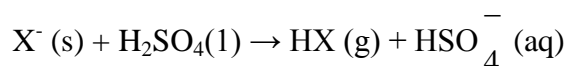


2. To the solution of the unknown, add aqueous solution of lead (II) ethanoate and boil the mixture. Formation of a brown precipitate of lead (IV) oxide confirms presence of the oxo chloride. This is because the oxo chloride oxidizes lead (II) to lead (IV) as follows:



i) Halides: Chloride (Cl^{-}), Bromide (Br^{-}) and Iodine (I^{-}) ions:

1. To the unknown solid add a few drops of concentrated sulphuric acid and warm if necessary.
 - i. Evolution of hydrogen chloride gas confirms Cl^{-}
 - ii. Evolution of hydrogen bromide confirms Br^{-} .
 - iii. Evolution of iodine vapour confirms I^{-} .



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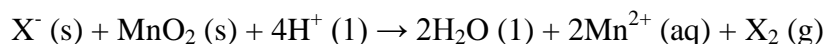
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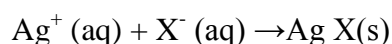
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2. To the unknown solid add some manganese (IV) oxide followed by concentrated sulphuric acid and heat.

- (i) Evolution of chlorine gas confirms Cl^-
- (ii) Evolution of bromine vapour confirms Br^-
- (iii) Evolution of iodine vapour confirms I^-

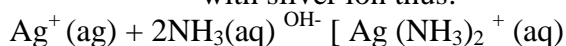


3. To a solution of the unknown, add 2 -3 drops of aqueous silver nitrate followed by excess dilute nitric acid. Formation of a precipitate of silver halide confirms presence of halide ion according to the equation.



NOTE:

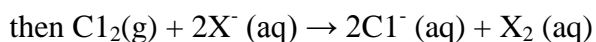
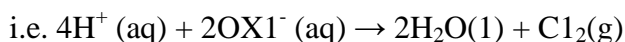
- i) The silver halides may be differentiated by their colours. AgCl is white, AgBr is pale yellow and AgI is yellow.
- ii) The Ag-X bond is not yet strong. The bond is broken by solar energy and therefore precipitates of the silver halides tend to darken on standing.
- iii) Silver chloride and silver bromide dissolve in excess aqueous ammonia. This is because the concentration of the silver ions required to precipitate AgCl and AgBr is greatly reduced in the presence of ammonia since ammonia forms a complex ion with silver ion thus:-



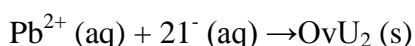
However AgI does not dissolve in aqueous ammonia because though the AgI is the least soluble, it provides still enough silver ions to cause the much lower solubility product of the halide to be exceeded.

3. To a solution of the unknown add bleaching powder then dilute nitric acid (or add chlorine water) followed by 2 =3 drops of tetra chloromethane.
- i) If the tetra chloromethane layer remains colourless, a Cl^- ion is confirmed.
 - ii) If a brown or red liquid forms in the tetra chloromethane layer, a Br^- ion is confirmed.
 - iii) If however a purple liquid develops in the tetra chloromethane layer, I^- ion is confirmed.

The acidified bleaching powder or chlorine water is an oxidizing agent. Free chlorine is therefore produced. It is the chlorine which oxidizes the bromide or iodine ions to their respective halogens. The halogens being covalent, separate in the organic solvent (tetra chloromethane), and therefore express their respective colours.

(Br⁻ or I⁻)

5. To a solution of the unknown halide, add aqueous solution of copper (II) ions (usually lead (II) ethanoate). A yellow precipitate of lead (II) iodine confirms presence of iodide ion,

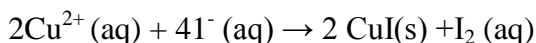


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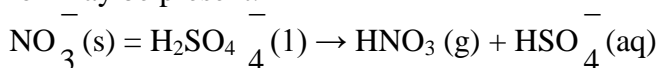
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5. To a solution of the unknown halide, add aqueous solution of copper (II) sulphate. Formation of a brown precipitate of copper (I) iodide confirms presence of iodide ion. This is a redox reaction.



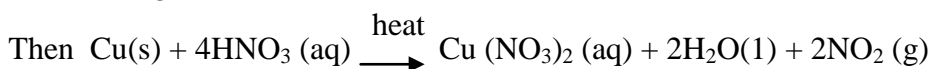
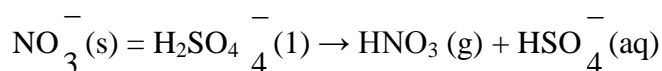
j) Nitrate: NO_3^{-} ion

1. To the unknown solid, add concentrated sulphuric acid and warm if necessary. Evolution of brown fumes which condense into an oily liquid at the sides of the test-tube indicates that a nitrate ion may be present.

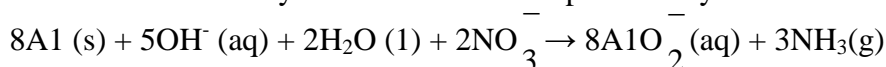


2. To an aqueous solution of the unknown, add an aqueous solution of freshly prepared iron (II) sulphate followed by a few drops of concentrated sulphuric acid added carefully down the sides of the test-tube. If a brown ring forms at the aqueous layer/acid junction, a nitrate is confirmed. (see under nitrite)

3. To the unknown, solid add a few pieces of copper turnings followed by about 5cm³ of concentrated sulphuric acid and heat the mixture. Evolution of brown fumes of nitrogen dioxide confirms a nitrate.



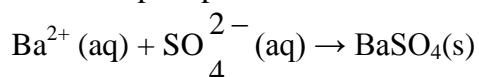
4. To a solution of the unknown (or solid) add some sodium hydroxide solution followed by zinc or aluminium powder and heat the mixture. Evolution of ammonia gas confirms a nitrate (see under Devarda's alloy test described under preliminary tests for anions).



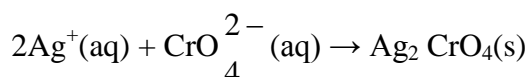
NOTE: This test requires exclusion of a nitrite.

k) Tetraoxo sulphur (VI), (Sulphate) ion: SO_4^{2-} :

1. To the solution of the unknown add aqueous barium nitrate followed by excess dilute nitric acid. A white precipitate insoluble in acid confirms a sulphate.



2. To the solution of the unknown, add aqueous silver nitrate followed by aqueous ammonia or nitric acid. A red precipitate soluble in both alkali and nitric acid confirms CrO_4^{2-} .



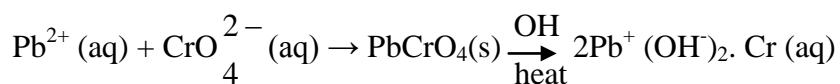
3. To the solution of the unknown, add aqueous lead (II) ethanoate followed by aqueous sodium hydroxide and boil. A yellow precipitate which turns red on boiling confirms chromate ion.

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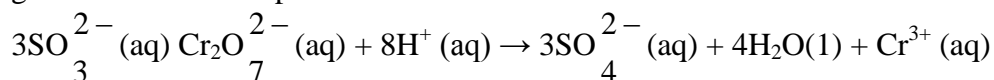
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Yellow

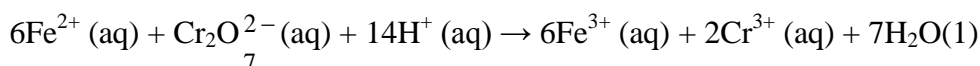
4. Dichromate ion is identified by using reducing agents in acid medium as exemplified below:

(i) To an aqueous solution of the unknown, add dilute sulphuric acid until the solution is acidic followed by some drops of sodium sulphide solution and heat. Colour change of orange $\text{Cr}_2\text{O}_7^{2-}$ to green Cr^{3+} confirms presence of dichromate ion.



The Cr^{3+} ion may be confirmed further using amyl alcohol (see under tests for Cr^{3+} ion).

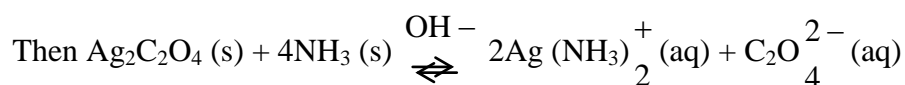
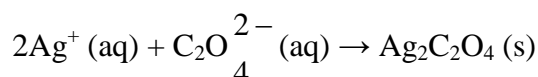
(ii) To an aqueous solution of the unknown, add dilute sulphuric acid drop-wise till the solution is acidic. Add a few drops of iron (II) chloride solution and heat. A deep red colouration which turns brown on boiling confirms presence of dichromate.



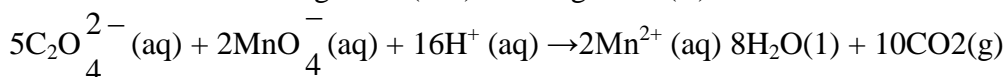
Note that any reagent that causes reduction of the dichromate ion could be used.

n) Ethanedioate (oxalate), $\text{C}_2\text{O}_4^{2-}$ ion:

1. To an aqueous solution of the unknown, add 2-3 drops of silver nitrate solution followed by excess aqueous ammonia. A white precipitate soluble in excess ammonia confirms ethanedioate ion.



2. To the solution of the unknown, add dilute sulphuric acid drop-wise until the solution is acidic. Heat the mixture to about 60°C ; just uncomfortable to touch. Then add drops of aqueous potassium manganate (VII) to the hot solution. If the manganate (VII) is immediately decolorized with gas bubbles, the ethanedioate is confirmed. This is because the ion reduces manganese (VII) to manganese (II) in acid medium thus:-



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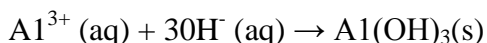
UNIT THREE
TESTS FOR CATIONS

Cations can be identified when they are in their aqueous solutions by converting them to their respective hydroxides. Most hydroxides, except those of NH_4^+ and Group I metal ions, are insoluble because of their strong basic characters. They are therefore usually identified by their colours when formed as precipitates. Some are amphoteric and so they dissolve in excess sodium hydroxide solution, which is a stronger base. Other cations form complexes with ammonia. Such cations form precipitates when treated with few drops of aqueous ammonia. But the precipitates so formed dissolve when excess ammonia solution is added.

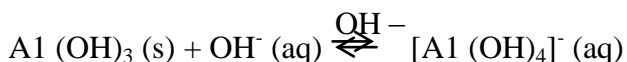
When hydroxide formation does not serve to completely distinguish a cation from others, more specific tests are necessary in order to CONFIRM the presence of the cation. The following tests are those often used in order to identify cations.

a) **Aluminium, Al^{3+} ion****1. With aqueous sodium hydroxide**

Add dilute sodium hydroxide solution drop-wise to an aqueous solution of the unknown until sodium hydroxide is in excess. A white gelatinous precipitate of aluminium hydroxide soluble in excess sodium hydroxide implies aluminium ion present.



Aluminium hydroxide is amphoteric so reacts with the stronger base to form a complex salt which is soluble.

**2. With aqueous ammonia**

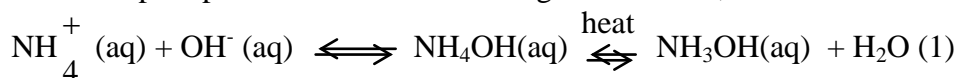
Aluminium hydroxide is formed as a white precipitate as in the case of sodium hydroxide above. However, the precipitate is insoluble in excess ammonia.

3. With Alizarin solution

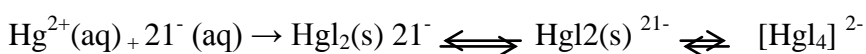
To the solution of the unknown, add aqueous ammonia drop-wise until the solution is alkaline; then add 1-2 drops of alizarin solution. A pink colouration confirms presence of aluminium ion.

b) **Ammonium, NH_4^+ ion****1. Reaction with aqueous sodium hydroxide**

To about 1cm^3 of a solution containing the unknown cation, add 2-3 drops of dilute sodium hydroxide and then continue adding sodium hydroxide drop-wise until it is in excess. Warm the mixture if no precipitate forms. If ammonia gas is evolved, ammonium ion is confirmed.

**2. With mercury (II) chloride**

To an aqueous solution of the unknown cation, add a few drops of mercury (II) chloride solution followed by potassium iodide solution added until the red precipitate of mercury (II) iodide just dissolves due to the formation of the tetraiodomercury (II) complex ion thus:



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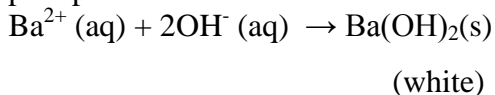
Now add aqueous sodium hydroxide until in excess. Formation of a yellow or brown precipitate or brown solution of oxydimercuriammonium iodide, $(\text{OH})_2 \text{NH}_2\text{I}$

C. Barium, Ba^{2+} ion

1. Flame test: Barium ion imparts a pale yellowish green colour to flame.

2. With aqueous NaOH

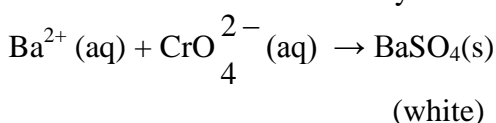
To the solution of the unknown, add aqueous sodium hydroxide drop-wise until in excess. A white precipitate insoluble in excess sodium hydroxide implies that barium ions may be present.



N.B: Does not form precipitate with aqueous ammonia *see under Ca^{2+}).

3. With dilute sulphuric acid (or Na_2SO_4)

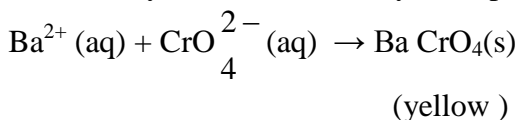
To the solution of the unknown add 2 – 3 drops of dilute sulphuric acid or sodium sulphate solution. Formation of a heavy white precipitate of BaSO_4 confirms presence of barium ions



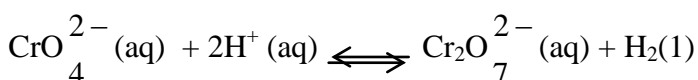
N.B Barium ion should be contrasted with lead (II) ion, which shows the same results. Use of aqueous sodium hydroxide may help.

4. With Chromate (IV) ions

To the aqueous solution of the unknown, add 2-3 drops of aqueous potassium chromate (VI) followed by ethanoic acid. A yellow precipitate insoluble in ethanoic acid confirms barium ions.



N.B: In acid solution the following equilibrium exists:



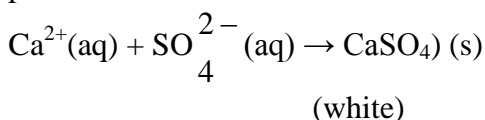
Even then, in the presence of dilute ethanoic acid, around $\text{PH}3$, there is still sufficient concentration of chromate ions to cause precipitation of barium (II) chromate; unlike calcium chromate, which is more soluble. Thus, although calcium ions may form a precipitate with chromate ions in case calcium ion is present in a fairly high concentration, the precipitate soon dissolves in ethanoic acid. Hence the difference between calcium and barium ions.

d) Calcium, Ca^{2+} ion

1. Flame test: Imparts a short lasting orange-red colour to flame.

2. With aqueous NaOH

To an aqueous solution of the unknown, add dilute sodium hydroxide solution drop-wise until in excess. A white precipitate insoluble in excess sodium hydroxide implies that calcium ion may be present.

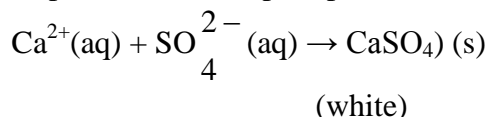


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N.B. Calcium ion does not form a precipitate with aqueous ammonia because ammonia is a weak base. So it does not provide hydroxide ions in sufficient quantity to exceed the solubility product of calcium hydroxide, which is quite high.

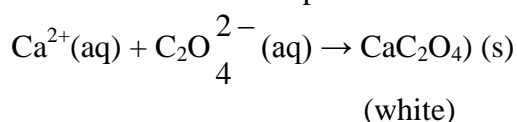
3. With dilute sulphuric acid or aqueous sodium sulphate

to the aqueous solution of the unknown, add 2-3 drops of dilute sulphuric acid (or aqueous sodium sulphate). A white precipitate of calcium sulphate confirms presence of the calcium ion.



4. With ammonium ethanedioate solution

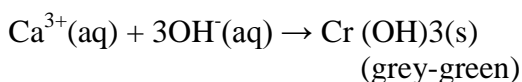
To the aqueous solution of the unknown, add aqueous ammonia until the solution is alkaline, then add a few drops of ammonium ethanedioate to the mixture. A white precipitate of calcium ethanedioate confirms presence of calcium ions.



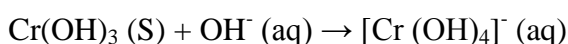
e) Chromium (III), Cr^{3+} ion

1. With sodium hydroxide

To the solution of the unknown, add aqueous sodium hydroxide drop-wise until in excess. A grey-green gelatinous precipitate soluble in excess sodium hydroxide to form a green solution implies chromium (III) ion



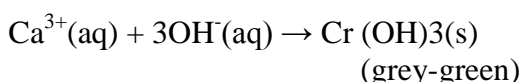
The chromium (III) hydroxide is amphoteric so reacts with the stronger base, sodium hydroxide, forming a soluble chromites salt.



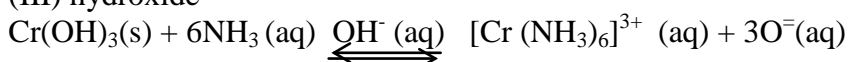
N.B: In this respect, chromium (III) resembles aluminium in Group III.

2. With dilute ammonia solution

To the solution of the unknown add a few drop of aqueous ammonium chloride followed by aqueous ammonia added drop-wise until ammonia is in excess. A green gelatinous precipitate soluble in excess ammonia solution to give a green solution implies chromium (III) ion.

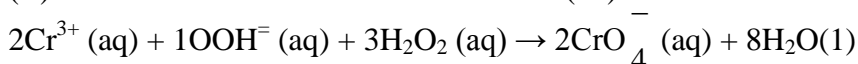


Chromium ion complexes with ammonia thus resulting into the observed dissolution of chromium (III) hydroxide



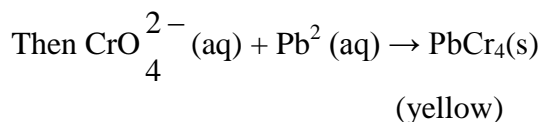
3. With hydrogen peroxide/lead (II) ethanoate

To the solution of the unknown add dilute sodium hydroxide until the solution is alkaline; then add hydrogen peroxide solution to the mixture followed by lead (II) ethanoate solution. A yellow solution formed on adding hydrogen peroxide which later gives a yellow precipitate when lead (II) ethanoate is added confirms chromium (III) ion.

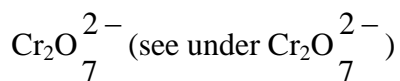


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N.B. Instead of adding lead (II) ethanoate to the resultant solution above, if amyl alcohol is added in small quantity followed by dilute sulphuric acid a blue colour would form in the alcohol layer, which confirms chromium(III) ion. The blue colour is due to chromium peroxide, CrO_5 , which is stabilized to some extent in organic solvent. It is also derived from chromium (VI) i.e.

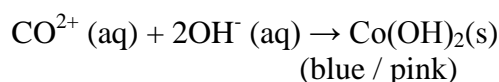


f) Cobalt (II), Co^{2+}

1. With aqueous sodium hydroxide

Add aqueous sodium hydroxide drop-wise to a solution of cobalt (II) until the alkali is in excess. Warm the mixture.

A blue ppt, which turns pink on warming in excess alkali indicates presence of cobalt (II) ion.



The ppt goes dark brown on standing due to oxidation of cobalt (II) hydroxide to cobalt (III) hydroxide by air (oxygen)

The ppt does not form when ammonium chloride is added prior to adding the aqueous alkali.

2. With aqueous ammonia

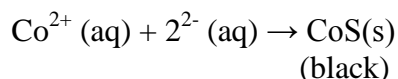
Add aqueous ammonia drop-wise to the suspected cobalt (II) ion solution; then add 2 – 3 drops of hydrogen peroxide solution.

A blue ppt soluble in excess ammonia or in aqueous ammonium chloride shows presence of cobalt (II) ion. The ammonia complexes with the cation. On standing or adding hydrogen peroxide, the ammoniacal solution turns red as various complexes are formed through oxidation.

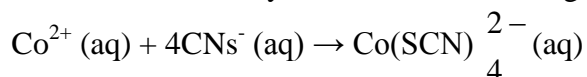
3. With aqueous ammonium sulphide

Add 2 -3 drops of aqueous ammonium sulphide to the suspect cobalt (II) solution.

Formation of a black ppt indicates presence of cobalt (II) ion.



The same reaction occurs when aqueous Co^{2+} ion solution is treated with aqueous ammonia or ammonium chloride followed by passage of hydrogen sulphide. The ppt of cobalt (II) sulphide is insoluble in dilute hydrochloric acid although it reacts slowly with hot conc. hydrochloric acid.



On adding amyl alcohol or either the blue colour separates into the organic layer.

5. Borax bead test

Heat a small loop of platinum wire to red hot and quickly use it to pick borax. Heat the borax in the loop of wire until it swells and forms a colourless transparent bead. Allow the bead to cool and spray it with a little water to moisten it. Use the moist bead to pick a MINUTE quantity of the suspected cobalt (II) compound. Heat the bead first in the reducing zone of the Bunsen burner and later in the oxidizing zone. A blue colour of the borax bead CONFIRMS cobalt (II) ion.

6. With potassium nitrate in the presence of ethanoic acid

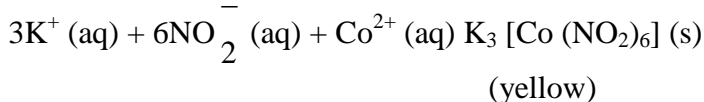
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Add ethanoic acid to an aqueous solution of cobalt (II) ion until the solution is acidic; then add 2 -3 drops of potassium nitrite solution and shake the mixture.

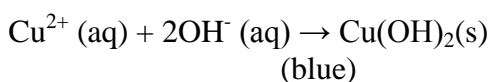
A yellow crystalline ppt confirms presence of cobalt (II) ion.



g) Copper (II), Cu^{2+} ion

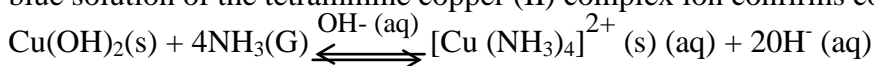
1. With sodium hydroxide

To the solution of copper (II), add sodium hydroxide drop-wise until in excess. A light blue (almost white) precipitate of copper (II) hydroxide insoluble in excess sodium hydroxide implies presence of copper (II) ion



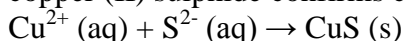
2. With aqueous ammonia

Add dilute ammonia solution to the solution of the unknown drop-wise until ammonia is in excess. A pale-blue precipitate of copper (II) hydroxide which dissolves in excess ammonia giving a deep blue solution of the tetrammine copper (II) complex ion confirms copper (II) ion.



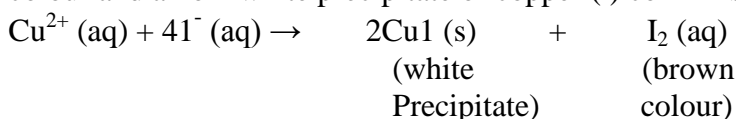
3. With hydrogen sulphide .

Add dilute hydrochloric acid to the solution of the unknown until the solution is acidic. Warm the mixture and pass hydrogen sulphide through the hot acidified mixture. A black precipitate of copper (II) sulphide confirms copper (II) ion.



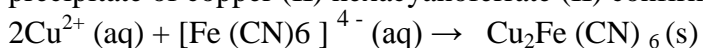
4. With potassium iodide

To the solution of the unknown add few drops of aqueous potassium iodide. formation of a brown colour and an off-white precipitate of copper (I) confirms presence of copper (II) ion.



5. With potassium hexacyanoferrate (II)

Add 2 -3 drops of aqueous potassium hexacyanoferrate to the solution of the unknown. A brown precipitate of copper (II) hexacyanoferrate (II) confirms presence of copper (II) ion.

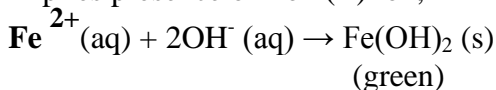


N.B. The reaction is a delicate test for copper(II) ion in solution. In very dilute solution only a purplish brown colour and no precipitate is obtained.

h) Iron (II), Fe^{2+} ion

1. With dilute sodium hydroxide

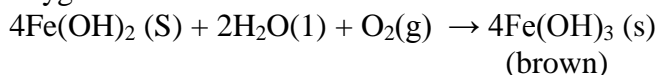
Add dilute sodium hydroxide drop-wise to a solution of the unknown until sodium hydroxide is in excess. A green gelatinous precipitate of iron (II) hydroxide insoluble in excess sodium hydroxide implies presence of iron (II) ion,



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Iron (II) hydroxide is purely basic and so does not dissolve in excess sodium hydroxide. But it slowly turns brown on exposure to air due to oxidation to iron (III) hydroxide by atmospheric oxygen.

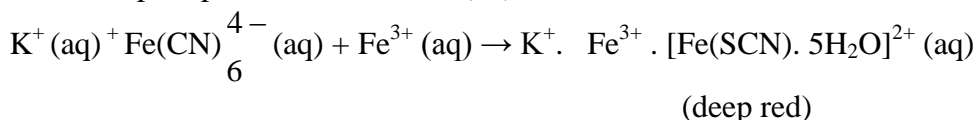


Iron (III) hydroxide, like iron (II) hydroxide is purely basic and therefore is not soluble in excess sodium hydroxide.

2. With aqueous ammonia same as for NaOH.

With potassium hexacyanoferrate (II)

To the solution of the unknown, add 2-3 drops of potassium hexacyanoferrate (II) solution. A dark blue precipitate confirms iron (III) ion.

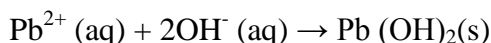


The rest is very sensitive but is negative with iron (II)

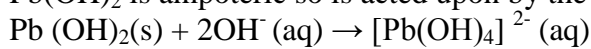
j) Lead (II), Pb^{2+} ion

1. With dilute NaOH

To the solution of the unknown, add dilute sodium hydroxide drop-wise till in excess. A white precipitate of lead (II) hydroxide soluble in excess sodium hydroxide implies lead (II) ions.

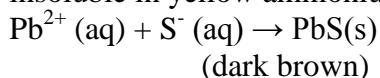


Pb(OH)_2 is amphoteric so is acted upon by the stronger base, NaOH, forming a soluble salt of lead.

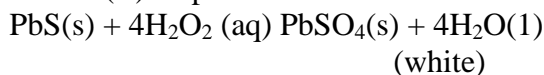


2. With Hydrogen sulphide

To the solution of the unknown, add dilute hydrochloric acid and then heat fairly strongly. As hydrogen sulphide through the hot acidified solution. A dark brown precipitate of lead (II) sulphide insoluble in yellow ammonium sulphide confirms lead (II) ion.

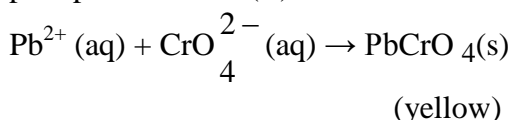


N.B. The precipitate turns white when treated with hydrogen peroxide due to oxidation of sulphide to lead (II) sulphate.



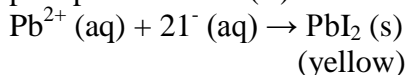
3. With potassium chromate

To the solution of the unknown, add 2-3 drops of aqueous potassium chromate. A yellow precipitate of lead (II) chromate confirms lead (II) ion.



4. With potassium iodide

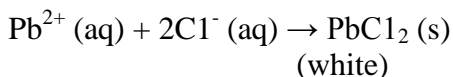
To the solution of the unknown, add 2-3 drops of aqueous potassium iodide. A yellow shiny precipitate of lead (II) iodide confirms lead (II) ion



5. With dilute hydrochloric acid (or aqueous sodium chloride)

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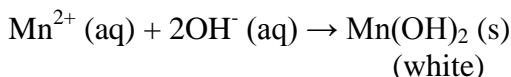
To the aqueous solution of the unknown, add 3 -4 drops of dilute hydrochloric acid or aqueous solution of sodium chloride. Heat the mixture. Formation of a white needle – like and shiny crystals of lead (II) chloride soluble in hot water but recrystallises on cooling confirms lead (II) ion.



k) Manganese (II), Mn^{2+} ion

1. With sodium hydroxide

To the solution of the unknown, add dilute sodium hydroxide solution drop wise till it is excess. An off-white precipitate of manganese (II) hydroxide formed, which is insoluble in excess sodium hydroxide implies presence of manganese (II) ion.

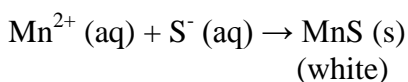


2. With dilute ammonia solution

Same observation as with sodium hydroxide.

3. With hydrogen sulphide

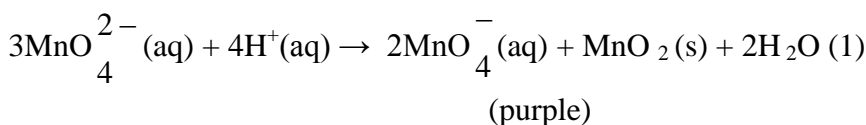
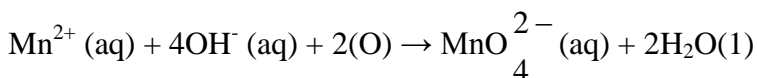
Add aqueous ammonia to the solution of the unknown until it is alkaline. Bubble hydrogen sulphide through the resultant solution. A dirty white or pink (flesh coloured) precipitate of manganese (II) sulphide implies presence of manganese (II) ion



4. With sodium bismuthate

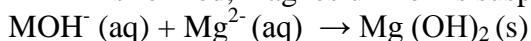
to the solution of the unknown (or solid) and few drops of concentrated nitric acid followed by a small quantity of solid sodium bismuthate and boil the mixture for some time. A violet (purple) colouration which forms and may settle as a precipitate confirms presence of manganese (II) ion.

The bismuthate and nitric acid are powerful oxidizing agents. They therefore oxidize manganese (II) to manganese (IV), which disproportionates to manganese (VII), which shows as the purple colouration.



l) Magnesium, Mg^{2+} ion

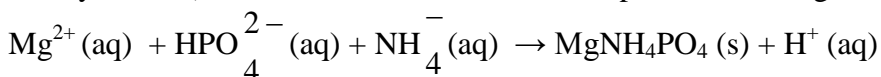
1. To the aqueous solution of the unknown cation, add aqueous hydroxide drop-wise until the sodium hydroxide is in excess. If a white precipitate insoluble in excess sodium hydroxide is formed, magnesium ion is suspected.



N.B. Similar observation is made with aqueous ammonia, although because of the weak basic character of ammonia, the precipitate may not show.

2. With disodium monohydrogen phosphate:

To the aqueous solution of the unknown, add solid ammonium chloride followed by 3-4 drops of di-sodium monohydrogen orthophosphate (sodium phosphate) then aqueous ammonia solution added till in excess. A white crystalline precipitate of magnesium ammonium phosphate (usually slowly formed) insoluble in ammonia confirms presence of magnesium ion.

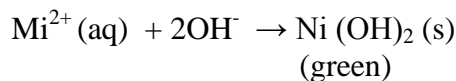


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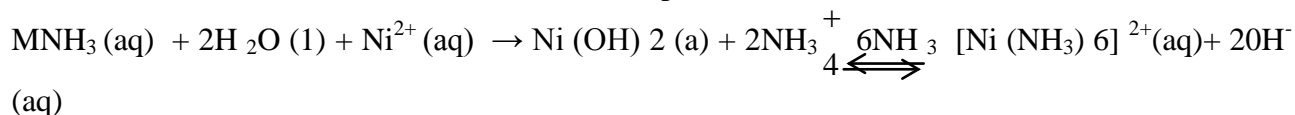
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m) Nickel (II) Ni^{2+} ion**1. With dilute sodium hydroxide**

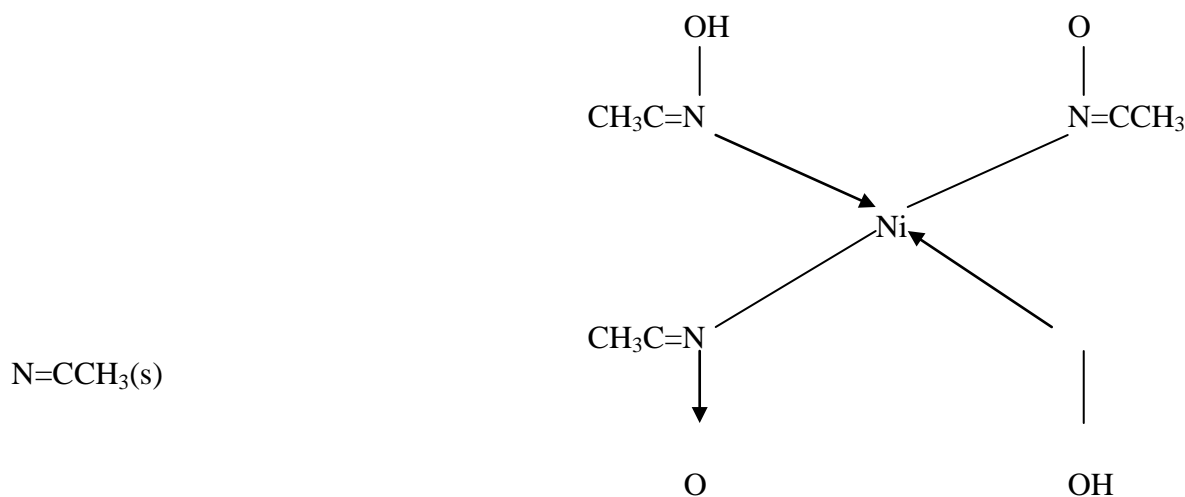
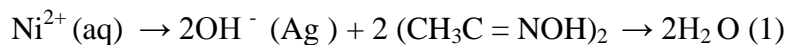
To the solution of the unknown, add dilute sodium hydroxide drop-wise until it is in excess. A light green precipitate of nickel (II) hydroxide insoluble in excess sodium hydroxide and does not change colour on heating implies presence of nickel (II) ion.

**2. With dilute ammonia solution**

Same precipitate as in the case of sodium hydroxide forms, but the precipitate dissolves in excess ammonia solution to give a blue solution due to complexation of nickel (II) ion with ammonia.

**3. With hydrogen sulphide**

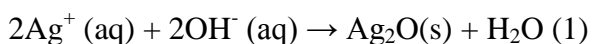
To the solution of nickel (II) ion add ammonia solution until the solution is alkaline; then pass hydrogen sulphide throughout the alkaline solution. A black precipitate of nickel (II) sulphide implies presence of nickel (II) ion.



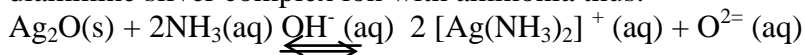
This is a delicate test for nickel (II) ion

n) Silver, Ag^{+} ion**1. With sodium hydroxide**

To the solution of the unknown, add aqueous sodium hydroxide drop-wise till in excess. A dark brown or black precipitate of silver oxide insoluble in excess sodium hydroxide implies silver ion.

**2. With aqueous ammonia**

Same compound precipitates as above but dissolves in excess ammonia because silver ion forms diammine silver complex ion with ammonia thus:-

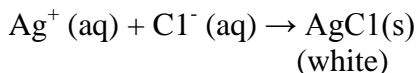
**3. With dilute hydrochloric acid**

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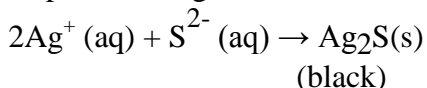
Add 2 – 3 drops of dilute hydrochloric acid (or chloride) solution to the solution of the unknown. a white precipitate which turns purple or dark in air and dissolves in ammonia solution confirms presence of silver ion.



The darkening is due to the partial decomposition of the weak Ag – Cl bond to metallic silver. It dissolves in ammonia due to the formation of the complex ion $[\text{Ag}(\text{NH}_3)_2]^+$ as seen above.

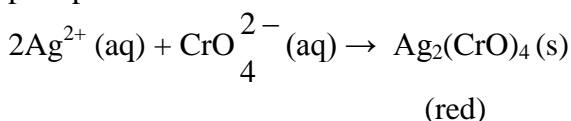
4. With hydrogen sulphide

To the solution of the unknown, add nitric acid until the solution is acidic and pass hydrogen sulphide through the acidified mixture. A black precipitate of silver sulphide confirms silver ion.



5. With potassium chromate

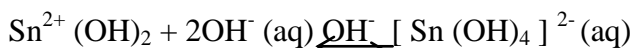
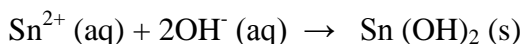
Add 2-3 drops of aqueous potassium chromate to the solution of the unknown. A dark red precipitate of silver chromate confirms silver ion.



o) Tin (II), Sn^{2+} ion

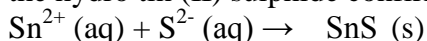
1. With dilute sodium hydroxide

To the solution of the unknown, add aqueous sodium hydroxide drop-wise till in excess. A white precipitate of tin (II) hydroxide soluble in excess due to its amphoteric nature implies presence of tin (II) ion.

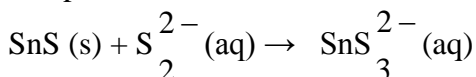


2. With aqueous hydrogen sulphide

To the solution of the unknown, add dilute hydrochloric acid until the solution is acidic. Heat the solution and bubble hydrogen sulphide into the solution while hot. A brown precipitate (probably the hydro tin (II) sulphide confirms presence of tin (II) ion

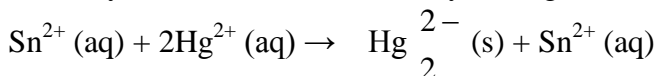


The precipitate dissolves in yellow ammonium sulphide due to oxidation of the tin (II) sulphide by the disulphide ion, S_2^{2-} contained in ammonium sulphide, forming the thiostannate ion SnS_3^{2-} a complex ion.

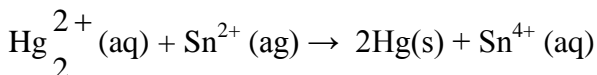


3. With aqueous mercury (II) chloride

To the solution of the unknown, add 2-3 drops of aqueous mercury (II) chloride. A white precipitate of mercury (I) chloride, which slowly turns grey confirms presence of tin (II) ion



Then excess $\text{Sn}^{2+} (\text{aq})$ reduce mercury (I) further to mercury (0), the grey metal



N.B: This indicate behaviour of tin (II) as a strong reducing agent.

4. With acidified $\text{KMnO}_4/\text{H}_2\text{S}$

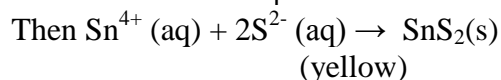
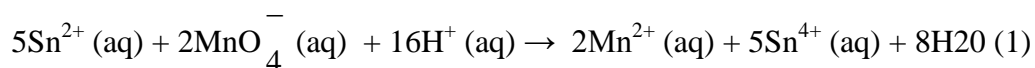
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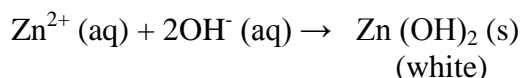
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To the aqueous solution of the unknown, add dilute sulphuric acid until the solution is acidic, followed by aqueous potassium manganate (VII) added until no further decolourisation of the manganate solution occurs. Pass hydrogen sulphide through the mix. Formation of a dirty yellow precipitate of tin (IV) sulphide confirms the presence of tin (II).

**P) Zinc, Zn^{2+} ion****1. With aqueous NaOH**

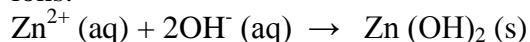
To the aqueous solution of the unknown, add dilute sodium hydroxide drop-wise until sodium hydroxide is in excess. A gelatinous white precipitate soluble in excess sodium hydroxide implies presence of zinc ions.



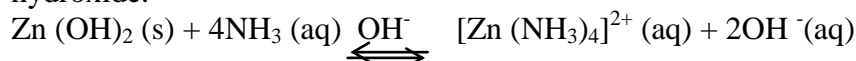
Zinc hydroxide is amphoteric. So it dissolves in excess sodium hydroxide because of the formation of the complex hydroxide ion thus:-

**2. With aqueous ammonia**

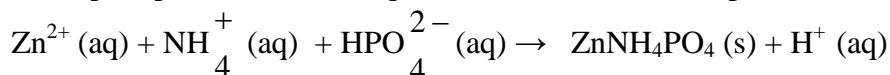
To the solution of the unknown, add aqueous ammonia drop-wise until ammonia is in excess. Formation of a white gelatinous precipitate soluble in excess ammonia implies presence of zinc ions.



Zinc ion forms complex, tetrammine Zinc (II) ion. This explains the dissolution of the zinc (II) hydroxide.

**3. With disodium mono hydrogen phosphate buffered solution**

To the solution of the unknown, add solid ammonium chloride followed by 2 -3 drops of disodium monohydrogen phosphate (sodium phosphate) solution followed by excess ammonia solution. A white precipitate soluble in aqueous ammonia confirms presence of zinc ions.



N.B the presence of aqueous ammonia causes the zinc ions to be largely converted to $[\text{Zn}(\text{NH}_3)_6]^{2+}$ thus reducing the concentration of Zinc (II) ions to the level below that required to reach and exceed the solubility product of the zinc ammonium phosphate thus the solid dissolves.

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UNIT FOUR

ORGANIC PROPERTIES

Introduction

Simple organic compounds are classified according to their functional groups. Functional groups are reactive centres in organic compounds, which typify reactions of a particular group or class of compounds.

Organic compounds may also be classified into ALIPHATIC and AROMATIC compounds. The following are some tests which are used for identifying organic compounds qualitatively.

Preliminary Tests

1) Flame Test

Most organic compounds are inflammable. Aliphatic compounds burn with non-sooty flame. Aromatic compounds burn with sooty flames.

Place a small quantity of the unknown compound in a crucible lid or on a spatula end and heat in a non luminous flame. Hold a glass tube or rod at the tip of the flame.

Observation

Substance burns with a non-sooty or clean flame

Substance burns with aluminous, sooty flame present

Or wit black solid carbon deposited on a cold surface.

Dedications

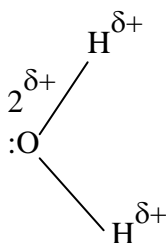
Aliphatic compound maybe present

An aromatic compound probably

ii) Solubilities

a) Solubility in water

Water is a polar solvent;



Hydrogen bonding occurs within its molecules to some extent. Some organic compounds dissolve in water because they can form hydrogen bonding with water molecules; for example alcohols.

Ionic compounds are more readily dissolved in water because the ions can be surrounded by polar water molecules. Some other compounds dissolve because they are hydrated into solution and the hydrate can enter into hydrogen bonding. These include alkanols.

To a small amount e.g 2 drops (if liquid) or a half a spatula end-full (if solid) of the unknown, add about 1cm³ of water and shake. If the substance dissolves, test the resultant solution with litmus paper or universal indicator.

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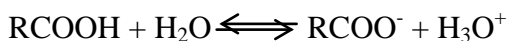
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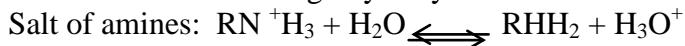
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- (i) If the aqueous solution is neutral, the original substance could be an alcohol, alkanal or alkanone.
- (ii) If the solution is acidic, the unknown could be a simple carboxylic acid, a salt of an amine, an acyl halide or an acid anhydride.

Acids are disassociated in water according to the equation



Other substances undergo hydrolysis in water as shown below:



- (iii) If the aqueous solution is alkaline, the unknown could be an amine, a salt of a carboxylic acid with a strong base. These substances undergo hydrolysis according to the equations shown below.

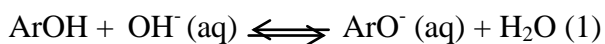
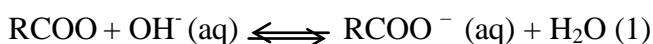


In practice salts are more readily soluble than carboxylic acids themselves.

b) Soluble in dilute (5%) sodium hydroxide

Organic compounds which are acidic in nature react with sodium hydroxide to form salts which are soluble in water. They will therefore dissolve in dilute sodium hydroxide solution.

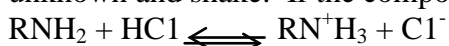
The procedure is to add aqueous sodium hydroxide to the unknown and shake. If the compound does not dissolve in water but dissolves in aqueous sodium hydroxide then a carboxylic acid or a phenol maybe suspected. The carboxylic acid and phenol are converted to their salts, which are soluble in water.



c) Solubility in dilute (5%) hydrochloric acid

Organic compounds which have basic functional groups will dissolve in dilute acids because they react with the acids to form salts which are soluble in water.

The practical procedure is to add about 1cm³ of dilute hydrochloric acid to a small quantity of the unknown and shake. If the compound is soluble, an amine may be suspected.



d) Solubility in aqueous sodium hydrogen carbonate

Phenols are weaker acids than carbonic acid. But carbonic acid is a stronger acid than carboxylic acid. As such, phenol will not liberate carbon dioxide from the hydrogen carbonate or carbonate whereas carboxylic acids will. So in order to distinguish between carboxylic acids and phenols, a little sodium hydrogen carbonate solution is added to the unknown. If the substance dissolves but without evolution of carbon dioxide, a phenol may be present. Otherwise a substance which dissolves is

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sodium hydrogen carbonate solution with carbon dioxide given out is most probably a carboxylic acid.

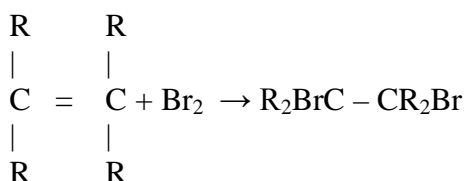
III) Reactions of some functional groups

a) With bromine in tetra chloromethane or bromine water

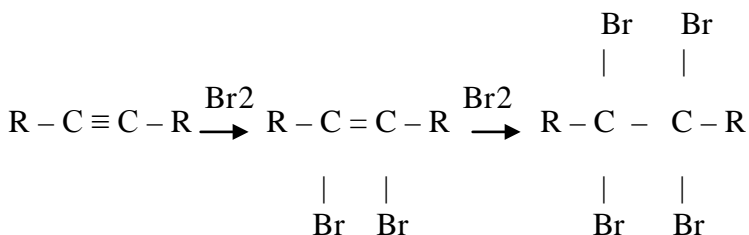
to the unknown substances, add 2-3 drops of bromine water. If bromine water is not decolourised, the unknown is most likely an alkenes. If bromine water is decolourised almost instantaneously, an alkene maybe present.

If decolourisation of bromine water occurs but rather more slowly, then the unknown may be alkynes.

Alkenes are saturated hydrocarbons. They are therefore generally uncreative. But alkenes contain at least one carbon-carbon double bond in their molecule. The un saturation enhances their reactions towards a number of electrophones. Thus bromine undergoes addition reaction very readily across the double bonds.



Alkynes, too, are unsaturated so will undergo addition of bromine across the C=C triple bonds. But because two moles of bromine are required instead of one in the case of the alkenes, the reaction is slower.

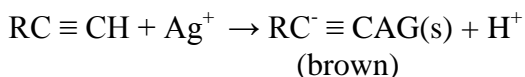


2. With alkaline potassium manganate (VII)

Add aqueous sodium carbonate to a solution of potassium manganese (VII) drop-wise until the solution is alkaline. Add 2-3 drops of the alkaline potassium manganate (VII) to a sample of the unknown. If the manganate colour is immediately changed from purple to colourless, it shows that the unknown may be un saturated compound (e.g. an alkene or an alkyne).

3. (i) Reaction with silver nitrate, add dilute ammonia

To an aqueous solution drop-wise until the precipitate which is formed dissolves. Add 2-3 drops of the ammoniacal solution to the unknown. A brown precipitate confirms the presence of alkynes.



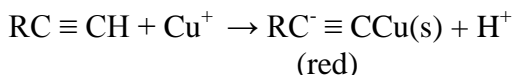
ii) Reaction with copper (I) chloride in aqueous ammonia

Repeat the test above, but use aqueous copper (II) chloride instead of silver nitrate.

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A red precipitate confirms the presence of an alkyne.



These reactions are used to differentiate alkynes with terminal triple bonds like but-1-yne ($\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}$) from alkynes with internal triple bonds like but-2-yne ($\text{CH}_3\text{C} \equiv \text{CCH}_3$). The precipitates, which are metal acetylides, form only with terminal alkynes.

b) Alcohols ($\text{R} - \text{OH}$) and Phenols (Ar-OH)

1. With litmus paper or universal indicator

Alcohols and phenols have hydroxyl ($-\text{OH}$) group as their typical functional group. Unlike phenols, which are acidic to litmus or universal indicator, aqueous solutions of alcohols are neutral to litmus and universal indicator.

2. With sodium metal.

To a sample of the unknown add a small piece of clean sodium metal. A vigorous effervescence with evolution of hydrogen may indicate presence of an alcohol.



When the resultant solution is evaporated to dryness and the residue is dissolved in water, an alkaline solution confirms sodium alkoxide formed from alcohol, thus giving sodium hydroxide in solution.



3. Luca's Test

Luca's reagent is a solution of anhydrous zinc chloride (1 mole) in concentrated hydrochloric acid (1 mole). Thus it may be prepared by dissolving (6.8g, 0.05 mol) of zinc chloride in concentrated hydrochloric acid (5.52g, 0.05 mole) with cooling in ice to avoid loss of hydrogen chloride. The solution should be kept between $26-27^\circ\text{C}$.

To 0.5cm^3 of alcohol in a test tube, add quickly 3cm^3 of Luca's reagent at $26 - 27^\circ\text{C}$, close the tube with a cork, shake well and allow to stand (preferably in ice water) and observe during 5 minutes. The following observations may be made.

- (i) If solution remains clear, though some darkening may occur, primary (I°) alcohol is present.
- (ii) If the clear solution becomes cloudy (a distinct upper layer formed after 1 hour), a secondary (II°) alcohol is present.
- (iii) If immediate reaction occurs and an insoluble cloudy layer forms at the surface within a few minutes. It means a tertiary (III°) alcohol is present.

Phenol shows no such result

4. Oxidation with acidified potassium dichromate solution

To a sample of the unknown, add about twice its volume of dilute sulphuric acid followed by 3 – 4 drops of aqueous potassium dichromate and heat the mixture gently.

The following observations may be made.

- (i) Rapid colour change from orange chromium (VI) to green chromium (iii) may mean presence of primary alcohol.

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- (ii) A rather slow colour change as above probably means secondary alcohol present.
- (iii) No apparent colour change means a tertiary alcohol probably present (see reduction properties of alcohols).

5. With iron (III) chloride solution

To an aqueous solution of the unknown, add 2 – 3 drops of iron (III) chloride solution. The following observations may be made. Formation of a violet or green colour confirms presence of phenol due to formation of a complex with iron (III) chloride. Otherwise if no colour change is seen despite other tests to indicate presence of – OH group, then the presence of alcohol is inferred.

6. Iodoform Test

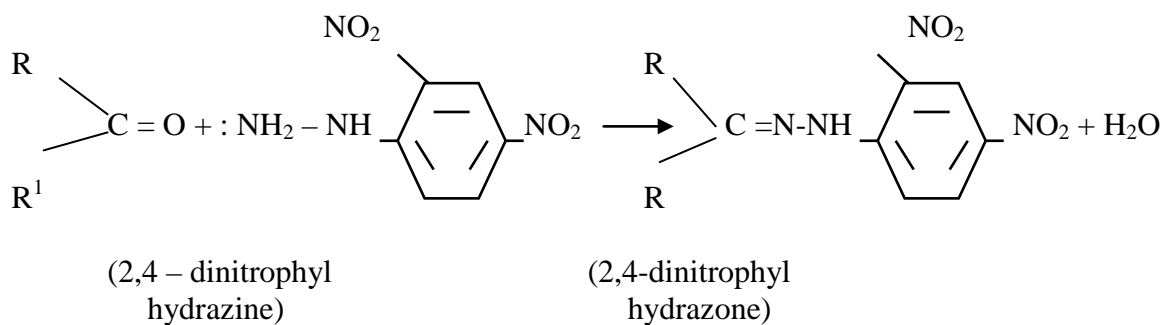
For alkanols (see under carbonyl compounds).



c) Carbonyl (-C-) compounds

These include alkanals, $\begin{array}{c} \text{O} \\ || \\ \text{R} - \text{C} - \text{H} \end{array}$ and ketones, $\begin{array}{c} \text{O} \\ || \\ \text{R} - \text{C} - \text{R} \end{array}$

- With Brady's reagent (2,3-dinitrophenylhydrazine; DNP) to 5 drops of the unknown, add 1-2 drops of 2,4 – dinitrophenylhydrazine solution, warm and dilute with water. A yellow or orange precipitate of 2,4-dinitrophenylhydrazone suggests the presence of a carbonyl group



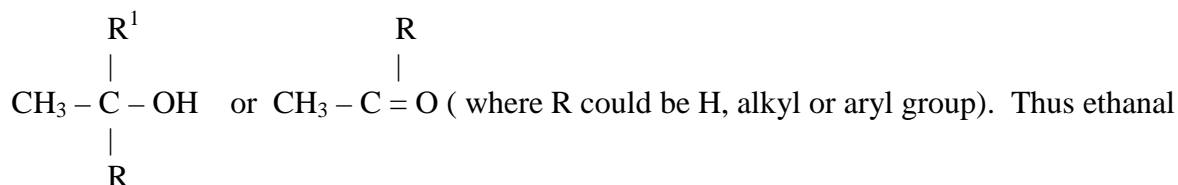
2.The iodoform reaction

To 5 drops of unknown, add 2 - 3 drops of aqueous potassium iodide followed by a freshly prepared solution of sodium hypochlorite until in excess. Warm the mixture gently. Or alternatively: to 5 drops of the unknown add 10 drops of a solution of iodine in aqueous potassium iodide followed by dilute sodium hydroxide added drop-wise until the brown colour just disappear or just turns pale yellow. Warm the mixture gently.

A pale yellow precipitate of triiodomethane (iodoform) forms which indicates the presence of a carbonyl compound of the structure RCOCH_3 . it is to be noted that iodoform test works for all compounds having the general formula.

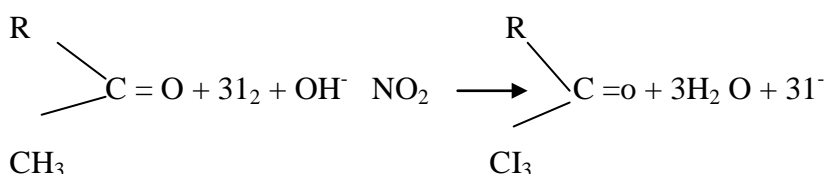
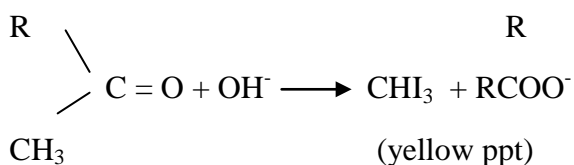
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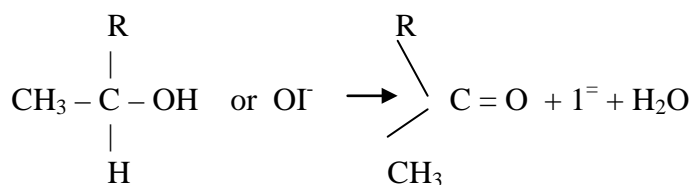
And ketones of the structure $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C} = \text{O} \\ \diagdown \\ \text{R} \end{array}$ show positive iodoform reaction

Iodoform reaction maybe considered as taking place in two stages as shown below.

i) **iodination**ii) **Cleavage**

Alcohols of the structure $\begin{array}{c} \text{R} \\ | \\ \text{CH}_3 - \text{C} - \text{R}_1 \\ | \\ \text{OH} \end{array}$ and ethanol also form iodoform. This is

Because they are first oxidized by iodine to the corresponding carbonyl compounds.

3. **Oxidation reactions**

Aldehydes are reducing agents (see theory). Whereas ketones resist oxidation by mild oxidizing agents like Fehling's solution and Tollen's reagent, aldehydes are readily oxidized by these reagents. Strong oxidizing agents like acidified potassium dichromate causes oxidation of the ketones by breaking carbon-carbon bonds and are not used in qualitative tests for those compounds.

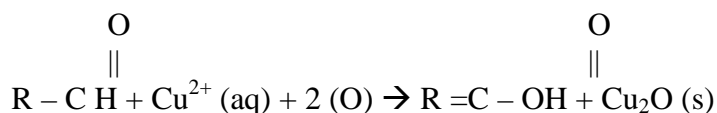
a) **With Fehling's solutions**

to the unknown, add 0.5 cm³ of Fehling's solution I, and 0.5 cm³ of Fehling's solution II and warm. Formation of a yellow or brown or red precipitate confirms presence of aldehyde.

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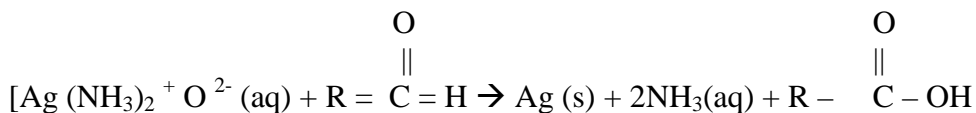
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b) With Tollen's reagent (Ammoniacal silver nitrate)

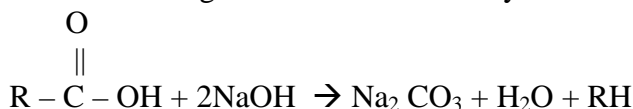
To about 5 drops of the unknown in a clean and dry test tube, add about 5 cm³ of ammoniacal silver nitrate solution (prepared by adding aqueous ammonia to silver nitrate solution until the precipitate of Ag₂O just dissolve). Boil the mixture. Formation of a silver mirror on the sides of the test tube confirms presence of an aldehyde.



c) Carboxylic acids, - $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} - \text{OH} \end{array}$

1. With soda -lime

To the unknown, add an excess of soda-lime and heat the mixture. Light any vapour that comes off. Evolution of gas which burns with a yellow flame confirms a carboxyl group.



Carboxylic acids and their salts undergo decarboxylation by soda-lime (basically sodium hydroxide) to produce hydrocarbons (RH), which burns.

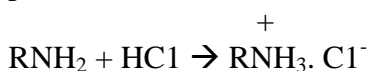
d) Amines; Primary (R – NH₂) and Secondary $\begin{array}{c} \text{R} \\ \diagup \\ \text{N} \\ \diagdown \\ \text{R} \end{array} \text{H}$

1. Solubility in water

The lower molecular mass amine are soluble in water and their aqueous solutions are basic to litmus.

2. Solubility in hydrochloric acid

Add about 1 cm³ of dilute hydrochloric acid to about 2 drops of the unknown in a test-tube and shake. If the substance dissolves readily without effervescence it probably means an amine is present.



3. Smell

Aliphatic amines are volatile and have characteristic ammonia – like or “fishy” smell. Primary amines smell rather more like ammonia itself (smell of goat's urine).

4. Reaction with sodium nitrite in hydrochloric acid

Dissolve 2 – 3 drops of the unknown in dilute hydrochloric acid and add concentrated hydrochloric acid drop-wise until the solution is acidic to litmus. Cool the solution in ice for about 15 minutes. Add ice cold 10% solution of sodium nitrite drop-wise and keep the mixture in an ice bath for about 10 minutes.

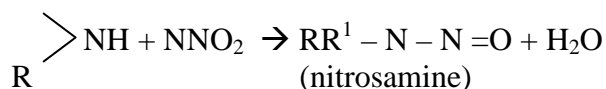
Primary aliphatic amines give clear solution with evolution of nitrogen gas.

Primary aromatic amines give clear solution and no evolution of nitrogen gas.

Secondary amines give yellow oil, (simple secondary aliphatic amines may form yellow solution).

The yellow oily liquid nitrosamine.

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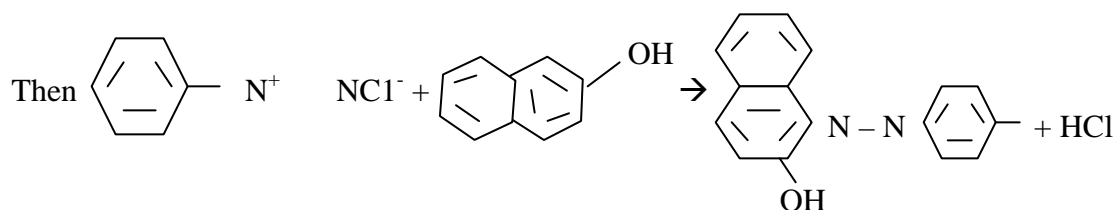
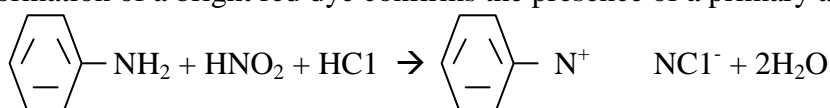


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Tertiary amines give clear solution. No nitrogen gas evolved.

5. Azo-dye formation

Take about 5 drops of the unknown in a test – tube and add concentrated hydrochloric acid drop-wise until the mixture is acidic. Add about 1 cm³ of sodium nitrite solution followed by 2 – 3 drops of 2 – naphthol (β-naphthol) solution in sodium hydroxide. (This solution may be prepared by dissolving a very small quantity of 2-naphthol in about 0.5 cm³ of sodium hydroxide solution). Formation of a bright red dye confirms the presence of a primary aromatic amine.



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1. Qualitative ORGANIC functional group tests in various homologous series			
TEST FOR	TEST METHOD	OBSERVATIONS	TEST CHEMISTRY and comments
ALKENE or alkyne i.e. any non-aromatic unsaturated hydrocarbon with a double or triple carbon-carbon bond.	Bubble gas through, or add liquid to, a solution of bromine in hexane or water.	The orange/brown bromine rapidly decolourises, as a saturated colourless organic bromo-compound is formed.	$R_2C=CR_2 + Br_2 \implies BrR_2C-CR_2Br$ $RC\equiv CR + 2Br_2 \implies Br_2RC-CRBr_2$ <p>R = H, alkyl or aryl</p> <p>Saturated alkanes give no fast reaction with bromine.</p>
Hydroxy group R-OH in alcohols and phenols (in 'dry' conditions*) The first 3 tests (i) - (iii) given on the right are quite general for most alcohols.	<p>(i) Mix it with a few drops of ethanoyl chloride, test fumes with litmus and silver nitrate (* note ethanoyl chloride reacts with water, phenols and amines too!).</p> <p>(ii) Mix it with a little phosphorus(V) chloride and test as above.</p> <p>(iii) Warm with a little ethanoic acid and a few drops of conc. sulphuric acid. Pour into water.</p>	<p>(i) Litmus turns red and a white precipitate with silver nitrate_(aq) (drop on end of glass rod), if the mixture is poured into water you may detect a 'pleasant' ester odour, can test for HCl but water and amines produce it too!</p> <p>(ii) as for (i) but no ester smell!</p> <p>(iii) You should get a 'pleasant' characteristic smell of an ester.</p>	<p>(i) $R-OH + CH_3COCl \implies CH_3COOR + HCl$</p> <p>An ester and hydrogen chloride are formed</p> <p>(ii) $R-OH + PCl_5 \implies R-Cl + POCl_3 + HCl$</p> <p>a chloro compound and hydrogen chloride are formed.</p> <p>(i) and (ii) $Ag^+_{(aq)} + Cl^-_{(aq)} \implies AgCl_{(s)}$ from the hydrogen chloride fumes dissolved in water.</p> <p>(iii) $CH_3COOH + ROH \implies CH_3COOR + H_2O$</p>
Primary alcohol RCH₂OH, R = H, alkyl or aryl (NOT a phenol). (ii) is not a good test on its own, since so many other readily reducible organic compounds will give the same reaction, though following it up by testing for an aldehyde gives it much more	<p>(i) Lucas test - shake a few drops with cold zinc chloride in conc. HCl_(aq)</p> <p>(ii) Distil with potassium dichromate(VI) and mod. conc. H₂SO_{4(aq)}</p>	<p>(i) Solution remains clear.</p> <p>(ii) If product distilled off immediately an aldehyde odour can be detected and the solution colour changes from orange to green.</p>	<p>(i) Not usually reactive enough to form a primary halogenoalkane</p> <p>(ii) $R-CH_2OH + [O] \implies R-CHO + H_2O$ or the full works! $3R-CH_2OH + Cr_2O_7^{2-} + 8H^+ \implies 2Cr^{3+} + 3R-CHO + 7H_2O$</p> <p>The orange dichromate(VI) ion is reduced to the green chromium(III) ion. If the organic product is collected you could test for an aldehyde.</p>

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validity.			
Secondary alcohol R_2CHOH , R = alkyl or aryl. (ii) is not a good test on its own,	(i) Lucas test. (ii) Distil with $K_2Cr_2O_7/H_2SO_{4(aq)}$	(i) Solution may cloud very slowly or remains clear (hit and miss) (ii) If product distilled off immediately a	(i) May be reactive enough to slowly form an insoluble secondary halogenoalkane: $R_2CHOH + HCl \Rightarrow R_2CHCl + H_2O$ (ii) $R_2CHOH + [O] \Rightarrow$
since so many other reducible organic compounds will give the same reaction, though following it up by testing for a ketone gives it much more validity.		ketone odour can be detected and the solution colour changes from orange to green.	$R-CO-R + H_2O$ or the full works! $3R_2CHOH + Cr_2O_7^{2-} + 8H^+ \Rightarrow 2Cr^{3+} + 3R-CO-R + 7H_2O$ The orange dichromate(VI) ion is reduced to the green chromium(III) ion. If the organic product is collected you could test for an aldehyde.
Tertiary alcohol R_3COH , R = alkyl or aryl.	(i) Lucas test. (ii) Distil with $K_2Cr_2O_7/H_2SO_{4(aq)}$	(i) Goes cloudy very quickly. (ii) No aldehyde or ketone readily formed	(i) Reactive enough to immediately form an insoluble tertiary halogenoalkane $R_3COH + HCl \Rightarrow R_3CCl + H_2O$ (iii) Stable to modest oxidation.
Phenols (OH group is attached directly to aromatic ring). $R-OH$, where R is aryl e.g. C_6H_5OH	Add a few drops of iron(III) chloride solution to a little of the phenol in water.	Usually gives a purple colour.	(see also <u>test for primary aromatic amines</u> - use it in reverse starting with a known primary aromatic amine!)
Carboxylic acids $RCOOH$	Mix the carboxylic acid with water and add a little sodium hydrogencarbonate solid or solution.	fizzing, colourless gas gives white precipitate with limewater	$RCOOH + NaHCO_3 \Rightarrow RCOONa + H_2O + CO_2$ (see also salts of aliphatic carboxylic acids below)
Salts of aliphatic carboxylic acids e.g. $RCOO^-Na^+$ or $(RCOO^-)_2Mg$ etc.	Add a little dilute hydrochloric/sulfuric acid to a suspected salt of an aliphatic carboxylic acid.	The solid or solution should have no strong odour, but after adding the mineral acid you should get a pungent odour of the original acid.	The stronger acid, HCl/H_2SO_4 displaces the weaker aliphatic carboxylic acid which have strong-pungent characteristic odours e.g. ethanoic acid from an ethanoate salt (<i>smell of acetic acid, vinegar</i>) and butanoates release butanoic acid (<i>butyric acid, rancid odour</i>).

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Acid or Acyl Chloride RCOCl Fumes in air forming $\text{HCl}_{(g)}$	<p>(i) Add a few drops to water, test with litmus and silver nitrate solution.</p> <p>(ii) Add to a little ethanol and pour the mixture into water.</p>	<p>(i) Litmus turns red and a white precipitate with silver nitrate.</p> <p>(ii) As above and you may detect a 'pleasant' ester odour.</p>	<p>(i) $\text{RCOCl} + \text{H}_2\text{O} \Rightarrow \text{RCOOH} + \text{HCl}$</p> <p>The acid chloride is hydrolysed to form HCl acid (chloride ions) and the original carboxylic acid.</p> <p>(ii) $\text{CH}_3\text{CH}_2\text{OH} + \text{RCOCl} \Rightarrow \text{RCOOCH}_2\text{CH}_3 + \text{HCl}$, an ethyl ester and hydrogen chloride are formed</p>
Acid Amide RCONH_2	Boil the suspected amide with dilute sodium hydroxide solution, see in inorganic for ammonia tests.	ammonia evolved on boiling (no heat required to form ammonia, if it was an ammonium salt)	$\text{RCONH}_2 + \text{NaOH} \Rightarrow \text{RCOONa} + \text{NH}_3$
Aliphatic amines (primary, where R = alkyl) R-NH₂ e.g. $\text{CH}_3\text{CH}_2\text{CH}_2\text{-NH}_2$	<p>(i) Lower members soluble in water but a very fishy smell! test with red litmus and conc. HCl(aq) fumes.</p> <p>(ii) If a suspected salt of an amine, then add sodium hydroxide solution to free the amine.</p>	<p>(i) A fishy odour, litmus turns blue, white clouds with HCl.</p> <p>(ii) The above is not observed until after adding the alkali.</p>	<p>(i) Unless its a liquid or solid, only the more fishy odour distinguishes it from ammonia.</p> <p>(ii) The reaction is e.g.</p> $\text{R-NH}_3^+ + \text{OH}^- \Rightarrow \text{R-NH}_2 + \text{H}_2\text{O}$
Aromatic amines (where R = aryl with the amine or amino group directly attached to an aromatic ring) R-NH₂ e.g. $\text{C}_6\text{H}_5\text{-NH}_2$	<p>(i) Dissolve the primary aromatic amine in dilute hydrochloric acid at 5°C and mix with sodium nitrite solution.</p> <p>(ii) Add a phenol dissolved in dilute sodium hydroxide.</p>	<p>(i) It should be a clear solution with few, if any, brown fumes.</p> <p>(ii) A coloured precipitate [red - brown - yellow etc.]</p>	<p>(i) If a primary aromatic amine, a 'stable' diazonium salt is formed. Diazonium salts from aliphatic amines decompose rapidly evolving colourless nitrogen.</p> <p>(ii) An azo dyestuff molecule is formed in a coupling reaction e.g.</p> $\text{C}_6\text{H}_5\text{-N=N-C}_6\text{H}_4\text{-OH}$
Aldehydes (R-CHO, R = H, alkyl or aryl) to distinguish from ketones ($\text{R}_2\text{C=O}$, R = alkyl or	(a) Add a few drops of the suspected carbonyl compound to Brady's reagent (2,4-dinitrophenylhydrazine solution)	(a) A yellow-orange precipitate forms with both types of carbonyl compound.	The aldehyde or ketone 2,4-dinitrophenylhydrazone is formed $\text{R}_2\text{C=O} +$

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<p>aryl) and also reducing sugars.</p> <p>Note</p> <p>(1) Test (b)(i) and (ii) can be used to distinguish aldehydes (reaction) and ketones (no reaction).</p> <p>(2) Aromatic aldehydes do NOT give a positive result with (b)(ii) Benedict's or Fehling's reagent).</p> <p>(3) Reducing sugars may also give a positive test with (b)(i)/(ii) reagent e.g. glucose (aldohexose) but not fructose? (ketohexose)?</p>	<p>(b)(i) warm a few drops of the compound with Tollens' reagent [ammoniacal silver nitrate]</p> <p>(b)(ii) simmer with Fehling's or Benedict's solution [a blue complex of $\text{Cu}^{2+}_{(\text{aq})}$]</p>	<p>(b) Only the aldehyde produces</p> <p>(i) A silver mirror on the side of the test tube.</p> <p>(ii) A brown or brick red ppt.</p>	<p>$(\text{NO}_2)_2\text{C}_6\text{H}_3\text{NHNH}_2 \implies$</p> <p>$(\text{NO}_2)_2\text{C}_6\text{H}_3\text{NHN}=\text{CR}_2 + \text{H}_2\text{O}$</p> <p>(R = H, alkyl or aryl)</p> <p>This tells you its an aldehyde or ketone, but can't distinguish them, read on below!</p> <p>Aldehydes are stronger reducing agents than ketones and reduce the metal ion and are oxidised in the process</p> <p>i.e. $\text{RCHO} + [\text{O}] \implies \text{RCOOH}$</p> <p>(i) reduction of silver(I) ion to silver metal</p> <p>$\text{RCHO} + 2\text{Ag}^+ + \text{H}_2\text{O} \implies \text{RCOOH} + 2\text{Ag} + 2\text{H}^+$</p> <p>(ii) reduction of copper(II) to copper(I) i.e. the blue solution of the Cu^{2+} complex changes to the brown/brick red colour of insoluble copper(I) oxide Cu_2O.</p> <p>$\text{RCHO} + 2\text{Cu}^{2+} + 2\text{H}_2\text{O} \implies \text{RCOOH} + \text{Cu}_2\text{O} + 4\text{H}^+$</p> <p>With (b)(i)/(ii) no reactions with ketones.</p>
<p>Haloalkanes (haloalkanes) R-X where R = alkyl, X = Cl, Br or I</p> <p>The halide is covalently bound (C-X bond), so the halogen X cannot react with the silver ion to form the ionic $\text{Ag}^+\text{X}^-_{(\text{s})}$ precipitate until it</p>	<p>(i) Warm a few drops of the haloalkane with aqueous ethanolic silver nitrate solution, the ethanol increases the solubility of the immiscible haloalkanes.</p> <p>(ii) Gently simmering a few drops with aqueous NaOH (may need to add ethanol to increase solubility and reaction rate). Add dilute nitric acid followed by</p>	<p>(i) Observe colour of precipitate and the effect of ammonia solution on it (for rest of details see the (i) notes for <u>chloride</u>, <u>bromide</u> and <u>iodide</u> tests above in inorganic)</p> <p>(ii) see the (i) notes as above for more details.</p>	<p>(i) $\text{AgNO}_3 + \text{RX} \implies \text{R-NO}_3? + \text{AgX}_{(\text{s})}$</p> <p>(ii) The sodium hydroxide converts the halogen atom into the ionic halide ion in a hydrolysis reaction.</p> <p>$\text{RX}_{(\text{aq})} + \text{NaOH}_{(\text{aq})} \implies \text{ROH}_{(\text{aq})} + \text{NaX}_{(\text{aq})}$</p> <p>then $\text{Ag}^+_{(\text{aq})} + \text{X}^-_{(\text{aq})} \implies \text{AgX}_{(\text{s})}$</p>

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is converted to the 'free' X^- ionic form. Note that aromatic halogen compounds where the X is directly attached to the ring, do NOT readily hydrolyse in this way and no AgX ppt. will be seen. Aromatic C-X is a stronger bond than aliphatic C-X.	aqueous silver nitrate solution.		The addition of dilute nitric acid prevents the precipitation of other silver salts or silver oxide (e.g. Ag_2O forms if solution alkaline).
Esters $RCOOR'$ R = H, alkyl or aryl R' = alkyl or aryl There is no simple test for an ester . Usually a colourless liquid with a pleasant 'odour'.	The ester can be reacted with saturated ethanolic hydroxylamine hydrochloride + 20% methanolic KOH and gently heated until boiling. Then mixture acidified with 1M $HCl_{(aq)}$ and $FeCl_{3(aq)}$ added dropwise.	Deep red or purple colour formed. The test depends on the formation of a hydroxamic acid $R-C(=NOH)OH$ which forms coloured salts with $Fe^{3+}_{(aq)}$ ion.	The reaction is also given by acid chlorides and acid anhydrides, and phenols give a purple colour with iron(III) chloride, so frankly, the test is not that good. This test is not likely to be expected
Iodoform test The formation of CHI_3, triiodomethane (or old name ' <i>iodoform</i> ').	$NaOH_{(aq)}$ is added to a solution of iodine in potassium iodide solution until most of the colour has gone. The organic compound is warmed with this solution.	A yellow solid is formed with the smell of an antiseptic, CHI_3 , triiodomethane, melting point $119^\circ C$.	This reaction is given by the alcohol ethanol CH_3CH_2OH and all alcohols with the 2-ol structure $-CHOH-CH_3$ and the aldehyde ethanal CH_3CHO and all ketones with the 2-one structure $R-CO-CH_3$ ('methyl ketones') Its a combination of halogenation and oxidation and is not a definitive test for anything, it just indicates a possible part of a molecules structure.

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2. INORGANIC Qualitative TESTS Cations and Acids			
TEST FOR	TEST METHOD	OBSERVATIONS	TEST CHEMISTRY- comments
Test for the Ammonium ion NH₄⁺	Add COLD sodium hydroxide solution to the suspected ammonium salt and test any gas above the solution with red litmus.	Smelly ammonia released! and red litmus turns blue , gentle warming helps BUT the ammonia should be released at room temperature.	Ammonia gas is evolved because alkali freess ammonia from its salts. $\text{NH}_4^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \Rightarrow \text{NH}_{3(\text{g})} + \text{H}_2\text{O}_{(\text{l})}$ The hydroxide ion removes a proton from the ammonium ion to release the ammonia.
Test for acids i.e. the aqueous hydrogen ion i.e. H⁺ or H₃O⁺ ion (note: to completely identify acids you need to test for the anion e.g. chloride for HCl hydrochloric or sulfate ion if sulfuric acid etc.)	(i) Litmus or universal indicator or pH meter. (ii) Adding a little sodium hydrogen carbonate powder.	(i) Litmus turns red , and, a variety of colours with univ. ind. strong - red, weak - yellow /orange, depending on strength of acid. (ii) Fizzing with any carbonate and test the gas to see if it is carbon dioxide - test for CO₂ .	(i) A pH meter reading gives a value of less than 7 , the lower the pH number the stronger the acid, the higher the H ⁺ concentration, (ii) $\text{HCO}_3^-_{(\text{aq})} + \text{H}^+_{(\text{aq})} \Rightarrow \text{H}_2\text{O}_{(\text{l})} + \text{CO}_{2(\text{g})}$ However, some salts can give acid or alkaline solutions but advanced acid-base theory is needed to explain this.
Testing for Positive metal cations with a flame test (see also below for <u>NaOH_(aq) and NH_{3(aq)} tests for metal ion</u> and <u>heating carbonates</u> too. This test can be done in a more precise and specific manner using an instrument called	The metal salt or other compound is mixed with concentrated hydrochloric acid and a sample of the mixture is heated strongly in a bunsen flame on the end of a cleaned nichrome wire (or platinum if you can afford it!)	Group 1: lithium Li/Li⁺ crimson	All colours are due to electronic excitations to a higher electronic energy levels. You see the light emitted as the electrons return to lower more stable electronic energy levels. This is the basis of atomic emission and absorption spectroscopy.
		Group 1: sodium Na/Na⁺ yellow (can be slightly orangeish)	
		Group 1: potassium K/K⁺ violet/lilac (crimson through cobalt blue glass)	
		Group 2: calcium Ca/Ca²⁺ brick (yellowish) red (light green through cobalt blue glass)	
		Group 2: strontium	

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<p>a spectroscope and the technique is called emission spectroscopy. Specific emission lines of a characteristic frequency are observed - a fingerprint pattern.</p>		<table><tr><td>Sr/Sr²⁺ crimson</td><td rowspan="3">Aluminium, magnesium, iron and zinc do not produce a useful identifying flame colours. Other metal flame colors in Group 1: rubidium - red and caesium/cesium - blue</td></tr><tr><td>Group 2: barium Ba/Ba²⁺ yellowish/apple green</td></tr><tr><td>Transition Metal: copper(II) Cu/Cu²⁺ blue (flashes of green too)</td></tr></table>	Sr/Sr²⁺ crimson	Aluminium, magnesium, iron and zinc do not produce a useful identifying flame colours. Other metal flame colors in Group 1: rubidium - red and caesium/cesium - blue	Group 2: barium Ba/Ba²⁺ yellowish/apple green	Transition Metal: copper(II) Cu/Cu²⁺ blue (flashes of green too)
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Transition Metal: copper(II) Cu/Cu²⁺ blue (flashes of green too)						
<p>Testing for positive metal cations via sodium hydroxide (NaOH) or ammonia (NH₃) solutions.</p> <p>Note:</p> <p>(1) Both are alkalis, giving hydroxide ions, OH⁻, in their solutions.</p> <p>(2) Aluminium, magnesium, iron and zinc do not produce a useful identifying flame colour.</p> <p>(3) A more advanced test to distinguish iron(II) ions, Fe²⁺ and iron(III) ions, Fe³⁺</p> <p>(i) If potassium hexacyanoferrate(III) solution is added to the suspected iron solution, iron(II) ions give a deep blue precipitate of Turnbull's blue.</p> <p>(ii) If potassium hexacyanoferrate(II) solution is added to the suspected iron solution, iron(III) ions give a deep blue precipitate of</p>	<p>Dilute sodium hydroxide (NaOH) solution is added to a solution containing the suspected ion.</p> <p>Both the precipitate formed and the effect of excess alkali are important observations.</p> <p>All precipitates are white, unless otherwise stated, and all tend to be gelatinous in nature.</p> <p>The test should be repeated with aqueous ammonia solution (NH₃, 'ammonium hydroxide').</p> <p>The observations with ammonia solution are usually similar, but not always, the same and the differences can be important clues as to the identity of the metal ion.</p> <p>ppt. = precipitate.</p> <p>More on some of these <u>hydroxide precipitates on the 3-d block Transition Metals Series</u> pages.</p>	<p>aluminium ion: Al³⁺_(aq) + 3OH⁻_(aq) ==> Al(OH)_{3(s)} gives a white precipitate</p> <p>of aluminum hydroxide, which is not soluble in excess of the weak alkali ammonia, but dissolves in the stronger base/alkali sodium hydroxide (amphoteric) to give a clear colourless solution.</p> <p>Al(OH)_{3(s)} + 3OH⁻_(aq) ==> [Al(OH)₆]³⁻_(aq) (amphoteric behaviour because it dissolves in acids too)</p> <p>calcium ion: Ca²⁺_(aq) + 2OH⁻_(aq) ==> Ca(OH)_{2(s)} gives a white precipitate</p> <p>of calcium hydroxide with sodium hydroxide IF the concentration of calcium ion is high. It is not soluble in excess of NaOH. No precipitate is formed with ammonia solution.</p> <p>magnesium ion: Mg²⁺_(aq) + 2OH⁻_(aq) ==> Mg(OH)_{2(s)} gives a white precipitate</p> <p>of magnesium hydroxide, which is not soluble in excess of either NH₃ or NaOH. You could distinguish Mg from Ca with a <u>flame test</u> or ammonia test above.</p> <p>copper(II) ion: Cu²⁺_(aq) + 2OH⁻_(aq) ==> Cu(OH)_{2(s)} gives a blue/turquoise ppt.</p> <p>of copper(II) hydroxide, which dissolves in excess ammonia to give a deep blue solution of an ammine complex, but copper(II) hydroxide is NOT soluble in excess NaOH.</p> <p>Cu(OH)_{2(s)} + 4NH_{3(aq)} ==> [Cu(NH₃)₄]²⁺_(aq) + 2OH⁻_(aq)</p> <p>iron(II) ion: Fe²⁺_(aq) + 2OH⁻_(aq) ==> Fe(OH)_{2(s)} gives a dark green precipitate</p> <p>of iron(II) hydroxide, which is not soluble in excess of NH₃ or NaOH. Darkens in air due</p>				

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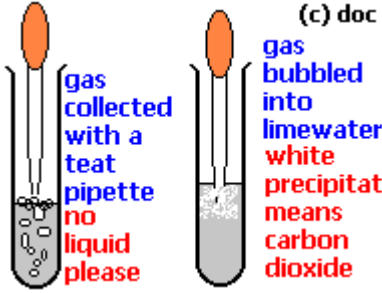
<p>Prussian blue.</p> <p>Note that Turnbull's blue is identical in composition to Prussian blue. For more chemical details see the <u>transition metals page on iron</u>.</p>	<p>to oxidation to $\text{Fe}(\text{OH})_3$.</p> <p>iron(III) ion: $\text{Fe}^{3+}_{(\text{aq})} + 3\text{OH}^{-}_{(\text{aq})} \rightleftharpoons \text{Fe}(\text{OH})_{3(\text{s})}$ forms a brown precipitate</p> <p>of iron(III) hydroxide, which is not soluble in excess of NH_3 or NaOH.</p> <p>Another test for iron(III) ions is to add a few drops of potassium/ammonium thiocyanate solution and a blood-red coloured compound is formed.</p> <p>zinc ion: $\text{Zn}^{2+}_{(\text{aq})} + 2\text{OH}^{-}_{(\text{aq})} \rightleftharpoons \text{Zn}(\text{OH})_{2(\text{s})}$ a white precipitate formed</p> <p>of zinc hydroxide, which dissolves in both excess (i) sodium hydroxide or (ii) ammonia to give a clear colourless solution:</p> <p>(i) $\text{Zn}(\text{OH})_{2(\text{s})} + 2\text{OH}^{-}_{(\text{aq})} \rightleftharpoons [\text{Zn}(\text{OH})_4]^{2-}_{(\text{aq})}$ (amphoteric behaviour because zinc hydroxide dissolves in acids too).</p> <p>(ii) $\text{Zn}(\text{OH})_{2(\text{s})} + 4\text{NH}_{3(\text{aq})} \rightleftharpoons [\text{Zn}(\text{NH}_3)_4]^{2+}_{(\text{aq})} + 2\text{OH}^{-}_{(\text{aq})}$ (soluble complex ion formation)</p> <p>chromium (III) ion: $\text{Cr}^{3+}_{(\text{aq})} + 3\text{OH}^{-}_{(\text{aq})} \rightleftharpoons \text{Cr}(\text{OH})_{3(\text{s})}$ a grey-green precipitate forms</p> <p>of chromium(III) hydroxide, which is soluble in excess of NaOH (amphoteric, dissolves in acids too) but not soluble in excess ammonia NH_3. With sodium hydroxide a dark green soluble hexahydroxo-complex ion is formed.</p> <p>$\text{Cr}(\text{OH})_{3(\text{s})} + 3\text{NaOH}_{(\text{aq})} \rightleftharpoons [\text{Cr}(\text{OH})_6]^{3-}_{(\text{aq})}$</p> <p>manganese(II) ion: $\text{Mn}^{2+}_{(\text{aq})} + 2\text{OH}^{-}_{(\text{aq})} \rightleftharpoons \text{Mn}(\text{OH})_{2(\text{s})}$ produces an off-white precipitate</p> <p>of manganese(II) hydroxide, which is NOT soluble in excess of NH_3 or NaOH and rapidly turns brown=>black in air due to oxidation to manganese(III) oxide Mn_2O_3 and then manganese(IV) oxide, MnO_2.</p> <p>lead(II) ion: $\text{Pb}^{2+}_{(\text{aq})} + 2\text{OH}^{-}_{(\text{aq})} \rightleftharpoons \text{Pb}(\text{OH})_{2(\text{s})}$ a white precipitate forms</p> <p>of lead(II) hydroxide, which dissolves in excess sodium hydroxide (amphoteric) to give a clear colourless solution but does not dissolve in excess ammonia solution.</p> <p>$\text{Pb}(\text{OH})_{2(\text{s})} + 2\text{OH}^{-}_{(\text{aq})} \rightleftharpoons [\text{Pb}(\text{OH})_4]^{2-}_{(\text{aq})}$ (amphoteric behaviour with NaOH as with zinc hydroxide which also dissolves in acids</p>
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		too) The barium ion, $\text{Ba}^{2+}_{(\text{aq})}$ does not give a hydroxide precipitate because barium hydroxide, $\text{Ba}(\text{OH})_2$, is too soluble.
MISCELLANEOUS CATION TESTS: (i) Lead(II) ion (ii) -	(i) add potassium iodide solution ==> yellow precipitate	(i) $\text{Pb}^{2+}_{(\text{aq})} + 2\text{I}^{-}_{(\text{aq})} \Rightarrow \text{PbI}_{2(\text{s})}$ a yellow precipitate of lead(II) iodide is formed
Metal Carbonates <u>See also carbonates and hydrogencarbonates.</u>	Sometimes heating a metal carbonate strongly to decompose it provides some clues to its identity. Adding acid to a carbonate ==> CO_2 and the colour of the resulting solution e.g. blue copper(II) ion $\text{Cu}^{2+}_{(\text{aq})}$, may also provide clues, but no good in most cases because most carbonates you come across are white giving colourless solutions except for some transition metals like copper, nickel and cobalt. The metal ion solution might also give a flame colour or a hydroxide precipitate with sodium hydroxide e.g. copper.	(i) copper(II) carbonate ==> copper(II) oxide + carbon dioxide $\text{CuCO}_{3(\text{s})} \Rightarrow \text{CuO}_{(\text{s})} + \text{CO}_{2(\text{g})}$ observations [green solid] ==> [black solid residue] + [colourless gas, test with limewater, white precipitate] (ii) zinc carbonate ==> zinc oxide + carbon dioxide $\text{ZnCO}_{3(\text{s})} \Rightarrow \text{ZnO}_{(\text{s})} + \text{CO}_{2(\text{g})}$ observations [white] ==> [solid residue, pale yellow hot, white cold] + [colourless gas, test with limewater ==> white precipitate]
Tests for NH_4^+ , $\text{H}^+/\text{H}_3\text{O}^+$, Li^+ , Na^+ , K^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Cu^{2+} , Al^{3+} , Mg^{2+} , Fe^{2+} , Fe^{3+} , Zn^{2+} , Cr^{3+} , Mn^{2+} , Pb^{2+} , CuCO_3 , ZnCO_3		

4. INORGANIC Qualitative TESTS Anions and Alkalis			
TEST FOR	TEST METHOD	OBSERVATIONS	TEST CHEMISTRY
Test for Carbonate ion CO_3^{2-} or hydrogencarbonate HCO_3^-	(i) Add any dilute strong acid to the suspected solid carbonate - if colourless gas	(i) Fizzing - colourless gas which turns limewater milky - cloudy fine white precipitate	(i) Any carbonate/hydrogencarbonate + acid ==> salt + water + carbon dioxide , then white precipitate with limewater. The

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 <p>Acid is added to the solid carbonate in a test tube. You could also collect a sample of gas from a heated carbonate, i.e. the solid is where the liquid is in the left hand test tube.</p> <p>Methods of gas preparation are described in more detail on another page.</p>	<p>given off, test with limewater.</p> <p>(ii) Effect of fairly strong heating and testing for any carbon dioxide given off.</p> <p>Test (ii) will distinguish sodium hydrogencarbonate (NaHCO₃ readily decomposes - 'baking powder') from anhydrous sodium carbonate (Na₂CO₃, thermally very stable).</p>	<p>(see above CO₂).</p> <p>(ii) There might be colour changes in the solid, but you need to collect a sample of gas from just above the heated solid to see it gives a white precipitate with limewater.</p> <p>Apart from hydrated sodium carbonate, sodium hydrogencarbonate is one of the few common carbonates to give off water on heating and condenses on side of test tube, but basic carbonates will also give off H₂O as well as CO₂.</p>	<p>ionic equations are for carbonate ...</p> $\text{CO}_3^{2-}(\text{s}) + 2\text{H}^+(\text{aq}) \Rightarrow \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$ <p>and for hydrogencarbonate ...</p> $2\text{HCO}_3^-(\text{s}) + 2\text{H}^+(\text{aq}) \Rightarrow \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$ <p>(ii) The thermal decomposition equations are for carbonates</p> $\text{MCO}_3(\text{s}) \Rightarrow \text{MO}(\text{s}) + \text{CO}_2(\text{g})$ <p>e.g. M = Mg, Zn, CuO and note that some give clear colour changes in the solid which might be useful to identify the metal (see heating carbonates in metal cation section)</p> <p>and for sodium hydrogencarbonate ...</p> $2\text{NaHCO}_3(\text{s}) \Rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$
<p>Sulphate ion or sulphate(VI) ion SO₄²⁻ [sulfate, sulfate(VI)]</p> <p>If the solution also contains the chloride ion, you test with barium ions 1st, filter off any barium sulphate precipitate and then <u>test for chloride ion</u>. This is because silver sulphate is also insoluble.</p>	<p>(i) To a solution of the suspected sulfate add dilute hydrochloric and a few drops of barium chloride/nitrate solution.</p> <p>(ii) Add lead(II) nitrate solution.</p>	<p>(i) A white precipitate of barium sulfate.</p> <p>(ii) A white precipitate of lead(II) sulphate.</p> <p>Test (i) is more definitive.</p>	<p>(i) $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \Rightarrow \text{BaSO}_4(\text{s})$</p> <p>Any soluble barium salt + any soluble sulphate forms a white dense barium sulphate precipitate.</p> <p>(ii) $\text{Pb}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \Rightarrow \text{PbSO}_4(\text{s})$</p> <p>Neither white precipitate is soluble in excess hydrochloric acid.</p>
<p>Sulphite ion or sulphate(IV) ion SO₃²⁻ [sulfite, sulfate(IV)]</p> <p>Test (iii) is easily unreliable, the sulphite ion is oxidised</p>	<p>(i) Add dilute hydrochloric acid to the suspected sulfite.</p>	<p>(i) Acidic choking sulfur dioxide gas formed.</p> <p>(ii) The dichromate paper</p>	<p>(i) Any sulphite salt + hydrochloric acid \Rightarrow chloride salt + sulphur dioxide.</p> <p>(ii) The sulphur dioxide</p>

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by air (dissolved oxygen) to give the sulphate ion, so you will be lucky to obtain a clear solution after adding excess acid.	<p>(ii) Test any gas evolved with fresh potassium dichromate(VI) paper.</p> <p>(iii) Add barium chloride or barium nitrate solution.</p>	<p>turns from orange to green.</p> <p>(iii) A white ppt. of barium sulphite which dissolves in excess hydrochloric acid to give a clear colourless solution.</p>	<p>reduces the dichromate(VI) to chromium(III). Note: sulphites do not give ppt. with acidified barium chloride/nitrate because sulphites dissolve in acids.</p> <p>(iii) $\text{Ba}^{2+}_{(\text{aq})} + \text{SO}_3^{2-}_{(\text{aq})} \Rightarrow \text{BaSO}_3(\text{s})$</p> <p>$\text{BaSO}_3(\text{s}) + 2\text{HCl}_{(\text{aq})} \Rightarrow \text{BaCl}_{2(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} + \text{SO}_{2(\text{aq})}$</p>
<p>Sulphide ion S^{2-} (sulfide)</p> <p>In test (ii) dangerous hydrogen sulphide (hydrogen sulfide) is formed.</p>	<p>(i) If soluble, add a few drops lead(II) ethanoate solution.</p> <p>(ii) If solid, add dil. $\text{HCl}_{(\text{aq})}$ acid, test smelly gas with damp lead(II) ethanoate paper (old name <i>lead acetate</i>).</p>	<p>(i) Black precipitate of lead sulphide.</p> <p>(ii) Rotten egg smell of hydrogen sulphide and the H_2S gas turns lead(II) ethanoate paper black.</p>	<p>(i) $\text{Pb}^{2+}_{(\text{aq})} + \text{S}^{2-}_{(\text{aq})} \Rightarrow \text{PbS}_{(\text{s})}$</p> <p>(ii) $\text{MS}_{(\text{s})} + 2\text{H}^{+}_{(\text{aq})} \Rightarrow \text{M}^{2+}_{(\text{aq})} + \text{H}_2\text{S}_{(\text{g})}$ (e.g. $\text{M} = \text{Pb, Fe, Cu, Ni}$ etc.) Then reaction (i) above occurs on the lead(II) ethanoate paper (old name <i>lead acetate</i>).</p>
<p>Chloride ion</p> <p>Cl^-</p> <p>If the solution also contains the sulphate ion, you <u>test with barium ions 1st</u>, filter off any barium sulphate precipitate and then test for chloride ion. This is because silver sulphate is also ~insoluble, so the two precipitates of silver sulfate and silver chloride could not be distinguished</p>	<p>(i) If the chloride is soluble, add dilute nitric acid and silver nitrate solution. The silver nitrate is acidified with dilute nitric acid to prevent the precipitation of other non-halide silver salts.</p> <p>(ii) If insoluble salt, add conc. sulphuric acid, warm if necessary then <u>test gas as for HCl</u>.</p> <p>(iii) Add lead(II) nitrate solution. Not a</p>	<p>(i) white precipitate of silver chloride soluble in dilute ammonia.</p> <p>(ii) You get nasty fumes of hydrogen chloride which turn blue litmus red and give a white precipitate with silver nitrate solution.</p> <p>(iii) A white ppt. of lead(II) chloride is formed.</p>	<p>(i) $\text{Ag}^{+}_{(\text{aq})} + \text{Cl}^{-}_{(\text{aq})} \Rightarrow \text{AgCl}_{(\text{s})}$</p> <p>Any soluble silver salt + any soluble chloride gives a white silver chloride precipitate, that darkens in light.</p> <p>(ii) $\text{Cl}^{-}_{(\text{s})} + \text{H}_2\text{SO}_{4(\text{l})} \Rightarrow \text{HSO}_4^{-}_{(\text{s})} + \text{HCl}_{(\text{g})}$,</p> <p>then $\text{Ag}^{+}_{(\text{aq})} + \text{Cl}^{-}_{(\text{aq})} \Rightarrow \text{AgCl}_{(\text{s})}$</p> <p>(iii) $\text{Pb}^{2+}_{(\text{aq})} + 2\text{Cl}^{-}_{(\text{aq})} \Rightarrow \text{PbCl}_{2(\text{s})}$</p>

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	very specific test - test (i) is best.		
Bromide ion Br⁻ Bromide and hydrogen bromide gas are harmful, irritating and corrosive substances.	<p>(i) If bromide soluble, add dilute nitric acid and silver nitrate solution. The silver nitrate is acidified with dilute nitric acid to prevent the precipitation of other non-halide silver salts.</p> <p>(ii) If insoluble salt, add conc. sulphuric acid, warm if necessary.</p> <p>(iii) Add lead(II) nitrate solution. Not a very specific test - test (i) is best.</p>	<p>(i) Cream precipitate of silver bromide, only soluble in concentrated ammonia.</p> <p>(ii) Orange vapour of bromine and pungent fumes of SO₂, test for sulphur dioxide.</p> <p>(iii) A white ppt. of lead(II) bromide is formed.</p>	<p>(i) $\text{Ag}^+_{(\text{aq})} + \text{Br}^-_{(\text{aq})} \Rightarrow \text{AgBr}_{(\text{s})}$</p> <p>Any soluble silver salt + any soluble bromide gives a cream silver bromide precipitate.</p> <p>(ii) The bromide ion is oxidised to bromine and the sulphuric acid is reduced to sulphur dioxide.</p> <p>(iii) $\text{Pb}^{2+}_{(\text{aq})} + 2\text{Br}^-_{(\text{aq})} \Rightarrow \text{PbBr}_{2(\text{s})}$</p>
Fluoride Ion F⁻ Fluoride and hydrogen fluoride gas are harmful, irritating and corrosive substances.	<p>(i) If the suspected fluoride is soluble add dilute nitric acid and silver nitrate solution.</p> <p>(ii) You can warm a solid fluoride with conc. sulphuric acid and hold in the fumes (ONLY!) a glass rod with a drop of water on the end.</p>	<p>(i) There is NO precipitate!</p> <p>(ii) Look for etching effects on the surface of the glass rod.</p>	<p>(i) Silver fluoride, AgF, is moderately soluble so this test proves little except that it isn't chloride, bromide and iodide!</p> <p>(ii) Hydrogen fluoride gas is produced by displacement</p> <p>$\text{F}^- + \text{H}_2\text{SO}_4 \Rightarrow \text{HSO}_4^- + \text{HF}$ which reacts with the glass silica to form silicic acid, silicon oxyfluoride, silicon fluoride. The chemistry is messy and complex BUT the glass rod is clearly etched.</p>

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Iodide ion I⁻	<p>(i) If iodide soluble, add dilute nitric acid and silver nitrate solution. The silver nitrate is acidified with dilute nitric acid to prevent the precipitation of other non-halide silver salts.</p> <p>(ii) If insoluble salt can heat with conc. sulphuric acid, (ii) get purple fumes of iodine and very smelly hydrogen sulphide.</p> <p>(iii) If iodide soluble, add lead(II) nitrate solution.</p>	<p>(i) Yellow precipitate of silver iodide insoluble in concentrated ammonia.</p> <p>(ii) purple vapour and rotten egg smell!</p> <p>(iii) Yellow precipitate of lead(II) iodide. Not too definitive -Test (i) best.</p>	<p>(i) $\text{Ag}^+_{(\text{aq})} + \text{I}^-_{(\text{aq})} \Rightarrow \text{AgI}_{(\text{s})}$, any soluble silver salt + any soluble iodide \Rightarrow silver iodide precipitate,</p> <p>(ii) iodide ion is oxidised to iodine and the sulphuric acid is reduced to 'rotten eggs' smelly hydrogen sulphide,</p> <p>(iii) insoluble lead(II) iodide formed</p> <p>$\text{Pb}^{2+}_{(\text{aq})} + 2\text{I}^-_{(\text{aq})} \Rightarrow \text{PbI}_{2(\text{s})}$</p>
Nitrate ion or nitrate(V) ion NO₃⁻	<p>(i) Boil the suspected nitrate with sodium hydroxide solution and fine aluminium powder (Devarda's Alloy) or aluminium foil.</p> <p>(ii) Add iron(ii) sulphate solution and then conc. sulphuric acid (the 'brown ring' test)</p> <p>(iii) Strongly heating nitrates of M²⁺ salts.</p>	<p>(i) the fumes contain ammonia, which turns red litmus blue, see ammonia test details</p> <p>(ii) Where the liquids meet a brown ring forms</p> <p>(iii) Nasty brown gas (beware!) of nitrogen (IV) oxide (nitrogen dioxide)</p>	<p>(i) The aluminium powder is a powerful reducing agent and converts the nitrate ion, NO₃⁻, into ammonia gas, NH₃</p> <p>(ii) NO complex of iron(II) formed</p> <p>(iii) a general thermal decomposition equation for this reaction is</p> <p>$2\text{M}(\text{NO}_3)_{2(\text{s})} \Rightarrow 2\text{MO}_{(\text{s})} + 4\text{NO}_{2(\text{g})} + \text{O}_{2(\text{g})}$</p> <p>where M = Pb, Zn, Mg, Cu etc.</p>
Nitrite ion or nitrate(III) ion NO₂⁻	No simple test to clearly i.d. it. (i) in acid solution it decomposes to give colourless NO gas which rapidly oxidises to nasty brown fumes of NO ₂ , (ii) it decolourises (purple \Rightarrow colourless) acidified potassium manganate(VII), (iii) it liberates		

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	iodine from acidified potassium iodide solution, (iv) forms ammonia with hot Al powder-foil/ $\text{NaOH}_{(\text{aq})}$ (see nitrate test) and gives 'brown ring' test - see nitrate tests above.		
Alkali: Hydroxide ion i.e. a soluble base (alkali) which forms the OH^- ion in water (note: to completely identify alkalis you need to test for the cation e.g. sodium for NaOH etc.)	<p>(i) Litmus or universal indicator or pH meter.</p> <p>(ii) Add a little of an ammonium salt.</p>	<p>(i) It turns litmus blue, variety of colours univ. ind. dark green - violet for weak - strong.</p> <p>(ii) If strongly alkaline ammonia should be released, see ammonia test for rest of details</p>	<p>(i) A pH meter gives a value of more than 7, the higher the pH number the stronger the alkali, the higher the OH^- concentration, (ii) ammonia gas is evolved:</p> <p>(ii) Ammonia released from the salt.</p> $\text{NH}_4^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \Rightarrow \text{NH}_{3(\text{g})} + \text{H}_2\text{O}_{(\text{l})}$
<p>Chromate(VI) ion</p> <p>CrO_4^{2-} (yellow)</p> <p>These tests are not very definitive, but collectively they are a good 'pointer'!</p>	<p>(i) Add dilute sulphuric acid.</p> <p>(ii) Add barium chloride/nitrate solution.</p> <p>(iii) Add lead(II) nitrate solution.</p>	<p>(i) The yellow solution turns orange as the dichromate(VI) ion is formed.</p> <p>(ii) A yellow precipitate of barium chromate(VI) is formed.</p> <p>(iii) A yellow precipitate of lead(II) chromate(VI) is formed. 'lead chromate'</p>	<p>(i) $\text{CrO}_4^{2-}_{(\text{aq})} + 2\text{H}^+_{(\text{aq})} \Rightarrow \text{Cr}_2\text{O}_7^{2-}_{(\text{aq})}$</p> <p>(ii) $\text{Ba}^{2+}_{(\text{aq})} + \text{CrO}_4^{2-}_{(\text{aq})} \Rightarrow \text{BaCrO}_{4(\text{s})}$</p> <p>(iii) $\text{Pb}^{2+}_{(\text{aq})} + \text{CrO}_4^{2-}_{(\text{aq})} \Rightarrow \text{PbCrO}_{4(\text{s})}$</p>
<p>Tests for $\text{CO}_3/\text{CO}_3^{2-}$, $\text{HCO}_3/\text{HCO}_3^-$, $\text{SO}_4/\text{SO}_4^{2-}$, $\text{SO}_3/\text{SO}_3^{2-}$, S_2^{2-}, F^-, Cl^-, Br^-, I^-, $\text{NO}_2/\text{NO}_2^-$, $\text{NO}_3/\text{NO}_3^-$, OH/OH^-, $\text{CrO}_4/\text{CrO}_4^{2-}$</p>			

END