Qualitative Analysis Part One: Cations

 Qualitative analysis is a structured set of methods used to determine the identities (but not the amounts) of the components that make up a mixture.





 Qualitative inorganic analysis is used to establish the presence or absence of particular elements or inorganic ions or compounds in an unknown sample. For example, an environmental technician might test a water sample to determine if arsenic, barium, or mercury is present.





 Qualitative organic analysis is used to establish the presence or absence of particular organic compounds or functional groups in an unknown sample. For example, a medical technician might test a urine sample to determine if glucose is present.



 In modern university and corporate laboratories, many qualitative analyses are done instrumentally, using methods such as infrared and mass spectroscopy, nuclear magnetic resonance, neutron activation analysis, x-ray diffraction, spectrophotometry, chromatography, electrophoresis, and others.



 Before such instruments were introduced, chemists did qualitative analyses using wet-chemistry procedures, reacting the unknown substance with various reagents and observing the results. Such wet-chemistry procedures remain important today, both for field tests or initial screening preliminary to instrumental analysis and as a learning tool.





A dead body has been found in the kitchen of a five star hotel. Upon close examination, the victim is found to have traces of a white powder under their fingernails. A brief survey of the kitchen reveals that containers of the following ingredients are easily assessable on the work surface. All five of the ingredients are identical in

appearance:

- Baking powder
 - Citric acid
 - Flour
 - Sugar
 - Table salt

You are the senior forensic scientist at the crime scene. As part of the investigation, you are required to identify the unknown white powder found under the victim's fingernails. Using your learning device, go online and research information on each ingredient. Give the name and formula of the active chemical that is present in each ingredient and state a qualitative test(s) for each chemical.

• Possible test for table salt (sodium chloride – NaCl): Add an aqueous solution of silver nitrate to an aqueous solution of the sodium chloride. A *white precipitate* of *silver chloride* will be observed. This confirms the presence of chloride ions in aqueous solution (all chlorides are soluble *except* silver chloride and lead(II) chloride): AgNO₃(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO₃(aq) Aq⁺(aq) + Cl⁻(aq) \rightarrow AgCl(s)

Note: A small amount of dilute nitric acid should be added to the white precipitate to ensure that it is silver chloride and *not silver carbonate*. Silver carbonate would react with the nitric acid to produce effervescence and the soluble salt, silver nitrate: $2HNO_3(aq) + Ag_2CO_3(s) \rightarrow 2AgNO_3(aq) + H_2O(l) + CO_2(g)$

There would be no observed reaction if the white precipitate was silver chloride.

Note: Silver ions can be used to test for chloride ions and chloride ions can be used to test for silver ions.



Possible test for sugar (sucrose – C₁₂H₂₂O₁₁):
 When solid sucrose is heated, it will undergo a thermal decomposition known as *caramelisation*, turning into a brown viscous liquid.
 Sucrose is a simple covalent molecule. Consequently, when dissolved in water, it will *not* conduct electricity as there are no mobile charge carrying particles present.

• **Possible test for flour** (starch – $(C_6H_{10}O_5)_n$):

Add an aqueous solution of iodine to the solid starch. The formation of a blue/black complex confirms the presence of starch.
Note: Just as iodine can be used to test for the presence of starch, starch can be used to test for the presence of iodine.



Possible test for baking powder

(sodium hydrogencarbonate – NaHCO₃):

Add dilute nitric acid to the solid baking powder. Effervescence will be observed as carbon dioxide gas is produced:

 $\begin{array}{rl} \mathsf{HC}l(\mathsf{aq}) \ + \ \mathsf{Na}\mathsf{HCO}_3(\mathsf{aq}) \ \rightarrow \ \mathsf{Na}\mathsf{C}l(\mathsf{aq}) \ + \ \mathsf{H}_2\mathsf{O}(l) \ + \ \mathsf{CO}_2(\mathsf{g}) \\ \mathsf{H}^+(\mathsf{aq}) \ + \ \mathsf{HCO}_3^{-}(\mathsf{aq}) \ \rightarrow \ \mathsf{H}_2\mathsf{O}(l) \ + \ \mathsf{CO}_2(\mathsf{g}) \end{array}$

The presence of carbon dioxide should be confirmed by bubbling the gas through limewater. A white precipitate of calcium carbonate will be observed:

$CO_2(g) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + H_2O(l)$ Note: Acids can be used to test for carbonates and hydrogencarbonates. Carbonates and hydrogencarbonates can be used to test for acids.



• Possible test for citric acid (citric acid $- C_6 H_8 O_7$):

The most straightforward test for an acid is to use either universal indicator paper / solution or blue litmus paper / solution. Firstly, the solid citric acid must be dissolved in distilled water so that it can exhibit its acidic properties. Blue litmus paper will turn red when dipped into the aqueous solution of citric acid.

Alternatively, an aqueous solution of sodium carbonate could be added to the aqueous solution of citric acid. Effervescence will be observed due to the production of carbon dioxide gas:

 $2H^+(aq) + CO_3^{2-}(aq) \rightarrow H_2O(l) + CO_2(g)$

The gas that is produced should be bubbled through limewater. The formation of a white precipitate confirms that the gas is carbon dioxide: $CO_2(g) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + H_2O(l)$









- Qualitative analysis is the *identification* of anions, cations and gases based upon their *unique chemical properties*.
 - Cations can be identified using the alkaline solutions aqueous sodium hydroxide and aqueous ammonia.
 - All cations (with the exception of Na⁺, K⁺ and NH₄⁺) produce *precipitates* with aqueous sodium hydroxide and aqueous ammonia.
 - The cation can then be identified by observing:
 i) The colour of the precipitate formed (important for the identification of transition metal cations).
 ii) Whether the precipitate is soluble or insoluble in an
- excess of the test reagent (important for the identification of cations of elements with amphoteric properties).



What is a precipitate? How is it different from a solution?



A precipitate is formed when two *clear solutions* react together to form an *opaque solid* product.

• All solutions are *clear*.

- Solutions may be coloured, e.g. we may refer to a "blue solution of copper(II) sulfate."
- All precipitates are *opaque*. There is no such thing as a clear precipitate!
 - Precipitates may be *coloured*, *e.g.* we may refer to a "yellow precipitate of lead(II) iodide."



Aqueous Silver Nitrate + Aqueous Sodium Chloride





Mixture of Aqueous Silver Nitrate and Aqueous Sodium Chloride





Ag⁺

Silver Chloride Precipitating from a Solution of Sodium Nitrate

















Sodium Ion

Chloride Ion

Water Molecule



Silver Chloride Precipitating from a Solution of Sodium Nitrate







Nitrate Ion

(Na⁺





Sodium Ion

Chloride Ion

Water Molecule



Qualitative Analysis Precipitate Formation White Precipitate of Silver Chloride









• The word equation for the reaction between aqueous silver nitrate and aqueous sodium chloride is:

Silver Nitrate + Sodium Chloride → Silver Chloride + Sodium Nitrate

 The balanced chemical equation for the reaction between aqueous silver nitrate and aqueous sodium chloride is:

 $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

• The ionic equation for the reaction between aqueous silver nitrate and aqueous sodium chloride is:

 $Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$

• Pay attention to the state symbols!



Qualitative Analysis Solubility Rules

- All ammonium salts are _____ in water.
- All potassium salts are _____ in water.
 - All sodium salts are _____ in water.
- All carbonates are _____ in water, except _____
 - All chlorides are _____ in water, except _____
 - All hydroxides are _____ in water, except _____
 - All nitrates are _____ in water.
 - All sulfates are _____ in water, except _____



Qualitative Analysis Solubility Rules

- All ammonium salts are <u>soluble</u> in water.
- All potassium salts are <u>soluble</u> in water.
 - All sodium salts are <u>soluble</u> in water.
- All carbonates are insoluble in water, except Na₂CO₃, K₂CO₃, (NH₄)₂CO₃
 - All chlorides are <u>soluble</u> in water, except <u>AgCl</u>, PbCl₂
- All hydroxides are insoluble in water, except NaOH, KOH, NH₄OH
 - All nitrates are <u>soluble</u> in water.
 - All sulfates are <u>soluble</u> in water, except <u>BaSO₄</u>, CaSO₄, PbSO₄



Determining the Products of a Reaction

The products of the precipitation reactions can be easily determined by *swapping the cations*:





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 $CuSO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + Cu(OH)_2(s)$ $FeCl_3(aq) + 3NH_4OH(aq) \rightarrow 3NH_4Cl(aq) + Fe(OH)_3(s)$

Quick test – what are the formulae of the following chemicals?

1) Aluminium hydroxide _____

2) Ammonium sulfate _____

3) Calcium hydroxide _____

4) Copper(II) sulfate _____

5) Iron(II) nitrate _____

6) Iron(III) chloride _____

7) lead(II) hydroxide _____

8) Zinc nitrate _____



Quick test – what are the formulae of the following chemicals?

1) Aluminium hydroxide $Al(OH)_3$

2) Ammonium sulfate $(NH_4)_2SO_4$

3) Calcium hydroxide $Ca(OH)_2$

4) Copper(II) sulfate CuSO₄

5) Iron(II) nitrate $Fe(NO_3)_2$

6) Iron(III) chloride $FeCl_3$

7) lead(II) hydroxide Pb(OH)₂

8) Zinc nitrate $Zn(NO_3)_2$



Writing Balanced Chemical and Ionic Equations

copper(II) nitrate + sodium hydroxide \rightarrow copper(II) hydroxide + sodium nitrate

 $Cu(NO_3)_2(aq) + NaOH(aq) \rightarrow Cu(OH)_2(s) + NaNO_3(aq)$

 $Cu(NO_3)_2(aq) + 2NaOH(aq) \rightarrow Cu(OH)_2(s) + 2NaNO_3(aq)$

lonic compounds that are dissolved in water can be split into their individual ions. This rule does not apply to insoluble solids:

$$Cu^{2+}_{(aq)} + 2NG_{3}^{-}_{(aq)} + 2NG_{(aq)}^{+} + 2OH_{(aq)}^{-} \rightarrow Cu(OH)_{2(s)} + 2NG_{(aq)}^{+} + 2NG_{3}^{-}_{(aq)} + 2NG_{3}^{-}_{(aq)}$$

Identify the ions that are responsible for formation of the *precipitate*, and delete the *spectator ions* from the equation:

$$Cu^{2+}(aq) + 2OH^{-}(aq) \rightarrow Cu(OH)_{2}(s)$$



Writing Balanced Chemical and Ionic Equations

lead(II) nitrate + potassium iodide \rightarrow lead(II) iodide + potassium nitrate

 $Pb(NO_3)_2(aq) + KI(aq) \rightarrow PbI_2(s) + KNO_3(aq)$ $Pb(NO_3)_2(aq) + 2KI(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$

lonic compounds that are dissolved in water can be split into their individual ions. This rule does not apply to insoluble solids:

$$\mathsf{Pb}^{2+}_{(\mathsf{aq})} + 2\mathsf{NG}_{3^{-}(\mathsf{aq})} + \mathsf{NG}_{(\mathsf{aq})} + 2\mathsf{I}_{(\mathsf{aq})} \to \mathsf{PbI}_{2(\mathsf{s})} + \mathsf{NG}_{(\mathsf{aq})} + 2\mathsf{NG}_{3^{-}(\mathsf{aq})}$$

Identify the ions that are responsible for formation of the *precipitate*, and delete the *spectator ions* from the equation:

$$Pb^{2+}(aq) + 2l^{-}(aq) \rightarrow Pbl_{2}(s)$$



Writing Balanced Chemical and Ionic Equations

aluminium chloride + aqueous ammonia \rightarrow aluminium hydroxide + ammonium chloride

 $AlCl_3(aq) + NH_4OH(aq) \rightarrow Al(OH)_3(aq) + NH_4Cl(aq)$

 $AlCl_3(aq) + 3NH_4OH(aq) \rightarrow Al(OH)_3(s) + 3NH_4Cl(aq)$

lonic compounds that are dissolved in water can be split into their individual ions. This rule does not apply to insoluble solids:

$$Al^{3+}_{(aq)} + 324_{(aq)} + 304_{(aq)} + 30H_{(aq)} \rightarrow Al(OH)_{3(s)} + 324_{(aq)} + 324_{(aq)$$

Identify the ions that are responsible for formation of the *precipitate*, and delete the *spectator ions* from the equation:

$$Al^{3+}(aq) + 3OH^{-}(aq) \rightarrow Al(OH)_{3}(s)$$


Qualitative Analysis A Note About State Symbols

(s) indicates that the chemical is a solid, e.g. sand is SiO₂(s)

(*l*) indicates that the chemical is a *liquid*,
 e.g. water is H₂O(*l*)

(g) indicates that the chemical is a gas,
e.g. carbon dioxide is CO₂(g)

(aq) indicates that the chemical is *dissolved in water*, *e.g.* an aqueous solution of sodium chloride is NaCl(aq)



Test for Cations Using Aqueous Sodium Hydroxide





Describe the use of *aqueous sodium hydroxide* and *aqueous ammonia* to identify the following aqueous cations:

- Aluminium cation Al³⁺(aq)
- Ammonium cation NH₄⁺(aq)
 - Calcium cation Ca²⁺(aq)
- Copper(II) cation Cu²⁺(aq)
 - Iron(II) cation Fe²⁺(aq)
 - Iron(III) cation Fe³⁺(aq)
 - Lead(II) cation Pb²⁺(aq)
 - Zinc cation Zn²⁺(aq)

Note: The formulae of complex ions are not required.



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• Remember that the qualitative tests are for *aqueous cations* and *not* for a *pure solid metal*.

• What does that mean...?

 If adding aqueous sodium hydroxide to an unknown solution results in the formation of a blue precipitate that is insoluble in excess reagent, *it confirms the presence of copper(II) cations in aqueous solution – Cu*²⁺(aq) – *not the presence of copper – Cu(s).*





Test for Al³⁺(aq) – Addition of NaOH(aq)





Qualitative Analysis Test for Al³⁺(aq) – Addition of NaOH(aq)



Aluminium Chloride + Sodium Hydroxide \rightarrow Aluminium Hydroxide + Sodium Chloride A $lCl_3(aq) + 3NaOH(aq) \rightarrow Al(OH)_3(s) + 3NaCl(aq)$ $Al^{3+}(aq) + 3OH^{-}(aq) \rightarrow Al(OH)_3(s)$

Qualitative Analysis Test for Al³⁺(aq) – Addition of NaOH(aq) excess aqueous aqueous sodium sodium hydroxide hydroxide NaOH_(aq) NaOH_(aq) 8 8 8 8 white aqueous precipitate aluminium of aluminium chloride hydroxide AICI_{3(aq)} $AI(OH)_{3(s)}$





The white precipitate of $Al(OH)_3$ dissolves in excess aqueous sodium hydroxide to produce a colourless solution.



Qualitative Analysis Test for $NH_4^+(aq) - Addition of NaOH(aq)$





Qualitative Analysis Test for $NH_4^+(aq)$ – Addition of NaOH(aq)





Qualitative Analysis Test for NH₄⁺(aq) – Addition of NaOH(aq)





Qualitative Analysis Test for NH₄⁺(aq) – Addition of NaOH(aq)



Ammonium Chloride + Sodium Hydroxide \rightarrow Sodium Chloride + Water + Ammonia $NH_4Cl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l) + NH_3(g)$ $NH_4^+(aq) + OH^-(aq) \rightarrow H_2O(l) + NH_3(g)$

Qualitative Analysis Test for Ca²⁺(aq) – Addition of NaOH(aq)





Qualitative Analysis Test for Ca²⁺(aq) – Addition of NaOH(aq)



Calcium Nitrate + Sodium Hydroxide \rightarrow Calcium Hydroxide + Sodium Nitrate Ca(NO₃)₂(aq) + 2NaOH(aq) \rightarrow Ca(OH)₂(s) + 2NaNO₃(aq) Ca²⁺(aq) + 2OH⁻(aq) \rightarrow Ca(OH)₂(s)

Qualitative Analysis Test for Ca²⁺(aq) – Addition of NaOH(aq)







The white precipitate of Ca(OH)₂ is insoluble in excess aqueous sodium hydroxide.



Qualitative Analysis Test for Cu²⁺(aq) – Addition of NaOH(aq)





Qualitative Analysis Test for Cu²⁺(aq) – Addition of NaOH(aq)





Qualitative Analysis Test for Cu²⁺(aq) – Addition of NaOH(aq)







The blue precipitate of Cu(OH)₂ is insoluble in excess aqueous sodium hydroxide.



Test for Fe²⁺(aq) – Addition of NaOH(aq)





Qualitative Analysis Test for Fe²⁺(aq) – Addition of NaOH(aq)



Iron(II) Sulfate + Sodium Hydroxide \rightarrow Iron(II) Hydroxide + Sodium Sulfate FeSO₄(aq) + 2NaOH(aq) \rightarrow Fe(OH)₂(s) + Na₂SO₄(aq) Fe²⁺(aq) + 2OH⁻(aq) \rightarrow Fe(OH)₂(s)

Qualitative Analysis Test for Fe²⁺(aq) – Addition of NaOH(aq)







The green precipitate of Fe(OH)₂ is insoluble in excess aqueous sodium hydroxide.



Qualitative Analysis Test for Fe²⁺(aq) – Addition of NaOH(aq)



Note: Iron(II) can oxidise to iron(III) upon exposure to atmospheric oxygen.

When this happens, the green precipitate of $Fe(OH)_2$ changes into a red-brown precipitate of $Fe(OH)_3$.



Test for Fe³⁺(aq) – Addition of NaOH(aq)





Qualitative Analysis Test for Fe³⁺(aq) – Addition of NaOH(aq)



Iron(III) Chloride + Sodium Hydroxide \rightarrow Iron(III) Hydroxide + Sodium Chloride FeC $l_3(aq) + 3NaOH(aq) \rightarrow Fe(OH)_3(s) + 3NaCl(aq)$ Fe³⁺(aq) + 3OH⁻(aq) \rightarrow Fe(OH)₃(s)

Qualitative Analysis Test for Fe³⁺(aq) – Addition of NaOH(aq)







The red-brown precipitate of $Fe(OH)_3$ is insoluble in excess aqueous sodium hydroxide.



Test for Pb²⁺(aq) – Addition of NaOH(aq)





Qualitative Analysis Test for Pb²⁺(aq) – Addition of NaOH(aq)



 $Pb(NO_3)_2(aq) + 2NaOH(aq) \rightarrow Pb(OH)_2(s) + 2NaNO_3(aq)$ $Pb^{2+}(aq) + 2OH^{-}(aq) \rightarrow Pb(OH)_2(s)$

Qualitative Analysis Test for Pb²⁺(aq) – Addition of NaOH(aq)







The white precipitate of Pb(OH)₂ dissolves in excess aqueous sodium hydroxide to produce a colourless solution.



Test for Zn²⁺(aq) – Addition of NaOH(aq)





Qualitative Analysis Test for Zn²⁺(aq) – Addition of NaOH(aq)



 $\begin{array}{l} \mbox{Zinc Nitrate + Sodium Hydroxide} \rightarrow \mbox{Zinc Hydroxide + Sodium Nitrate} \\ \mbox{Zn(NO}_3)_2(aq) \ + \ 2NaOH(aq) \ \rightarrow \ \mbox{Zn(OH)}_2(s) \ + \ 2NaNO_3(aq) \\ \hline \mbox{Zn}^{2+}(aq) \ + \ 2OH^-(aq) \ \rightarrow \ \mbox{Zn(OH)}_2(s) \end{array}$
Qualitative Analysis Test for Zn²⁺(aq) – Addition of NaOH(aq)







The white precipitate of Zn(OH)₂ dissolves in excess aqueous sodium hydroxide to produce a colourless solution.





Summary – Test for Cations Using Aqueous Sodium Hydroxide

Cation	Effect of Aqueous Sodium Hydroxide
Aluminium cation – Al ³⁺ (aq)	White ppt., soluble in excess giving a colourless solution.
Ammonium cation – NH ₄ +(aq)	Ammonia produced on warming.
Calcium cation – Ca ²⁺ (aq)	White ppt., insoluble in excess.
Copper(II) cation – Cu ²⁺ (aq)	Light blue ppt., insoluble in excess.
Iron(II) cation – Fe ²⁺ (aq)	Green ppt., insoluble in excess.
Iron(III) cation – Fe ³⁺ (aq)	Red-brown ppt., insoluble in excess.
Lead(II) cation – Pb ²⁺ (aq)	White ppt., soluble in excess giving a colourless solution.
Zinc cation – Zn ²⁺ (aq)	White ppt., soluble in excess giving a colourless solution.



Summary – Test for Cations Using Aqueous Sodium Hydroxide

"Chunk" your thinking to help you remember:

• *Cu*²⁺(*aq*), *Fe*²⁺(*aq*) and *Fe*³⁺(*aq*) form *coloured precipitates* which are *insoluble* in excess aqueous sodium hydroxide. **Note:** *copper* and *iron* are both *transition metals*.

 Al³⁺(aq), Pb²⁺(aq) and Zn²⁺(aq) form white precipitates which dissolve in excess aqueous sodium hydroxide to produce colourless solutions. Note: Al³⁺(aq), Pb²⁺(aq) and Zn²⁺(aq) are described as amphoteric which means they demonstrate both acidic and basic character.

• *Ca*²⁺(*aq*) forms a *white precipitate* which is *insoluble* in excess aqueous sodium hydroxide.

• *NH*₄⁺(*aq*) reacts with aqueous sodium hydroxide to form *ammonia gas* which turns moist red litmus



paper *blue* when the reaction is warmed gently.



Summary – Test for Cations Using Aqueous Sodium Hydroxide







Test for Cations Using Aqueous Ammonia





Ammonia gas is very soluble in water. Approximately
500 g of ammonia will dissolve in 1000g of water at 25 °C.



 When ammonia gas dissolves in water, some of the ammonia molecules and water molecules react to form an alkaline solution of ammonium hydroxide.

ammonia + water \rightleftharpoons ammonium hydroxide NH₃(g) + H₂O(l) \rightleftharpoons NH₄OH(aq)



Qualitative Analysis Aqueous Ammonia – NH₃(aq)

Aqueous ammonia is a solution of ammonia gas dissolved in water.

When ammonia gas is bubbled into water, some of the ammonia reacts with the water to form an aqueous solution of ammonium hydroxide – NH₄OH(aq):

 $NH_3(g) + H_2O(l) \rightleftharpoons NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

As a consequence of this, an aqueous solution of ammonia is actually a mixture of *ammonia molecules* (NH₃), *water molecules* (H₂O), *ammonium ions* (NH₄⁺) and *hydroxide ions* (OH⁻).

Note: The hydroxide ions can react with soluble metal cations to produce precipitates of the insoluble metal hydroxide.



• What is the essential difference between aqueous ammonia and aqueous sodium hydroxide?

• Aqueous sodium hydroxide is a *strong alkali*. This means that it *completely ionises* when dissolved in water:

 $NaOH(s) \rightarrow Na^{+}(aq) + OH^{-}(aq)$

 Aqueous ammonia is a weak alkali. Ammonia molecules only partially react and ionise in water to form ammonium hydroxide:

 $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$



 The consequence is that 1.00 mol/dm³ aqueous sodium hydroxide and 1.00 mol/dm³ aqueous ammonia contain *different* concentrations of hydroxide ions.

 \rightarrow 1.00 mol/dm³ aqueous sodium hydroxide contains 1.00 mol/dm³ hydroxide ions.

 \rightarrow 1.00 mol/dm³ aqueous ammonia contains approximately 0.004 mol/dm³ hydroxide ions.

 Reactions that take place when aqueous sodium hydroxide is used may *not* take place when aqueous ammonia is used, because the concentration of hydroxide ions in the aqueous ammonia is too low for a reaction to occur.



 When aqueous sodium hydroxide is added to Ca²⁺(aq), the relatively high concentration of OH⁻(aq) ensures that sufficient Ca(OH)₂(s) is formed to precipitate from the solution.

 However, when aqueous ammonia is added to Ca²⁺(aq), the relatively low concentration of OH⁻(aq) means that not enough Ca(OH)₂(s) is formed for a precipitate to be formed.

 For a similar reason, Al(OH)₃(s) and Pb(OH)₂(s) both dissolve in excess aqueous sodium hydroxide, but are both insoluble in excess aqueous ammonia.



Qualitative Analysis Test for $Al^{3+}(aq) - Addition of NH_3(aq)$





Qualitative Analysis Test for $Al^{3+}(aq) - Addition of NH_3(aq)$











The white precipitate of $Al(OH)_3$ is insoluble in excess aqueous ammonia.



Qualitative Analysis Test for Ca²⁺(aq) – Addition of NH₃(aq)





Qualitative Analysis Test for Ca²⁺(aq) – Addition of NH₃(aq)



There is no observed reaction between the calcium nitrate and aqueous ammonia – no precipitate is formed.









There is no observed reaction between the calcium nitrate and aqueous ammonia – no precipitate is formed.



Qualitative Analysis Test for Cu²⁺(aq) – Addition of NH₃(aq)





Qualitative Analysis Test for Cu²⁺(aq) – Addition of NH₃(aq)









The blue precipitate of $Cu(OH)_2$ dissolves in excess aqueous ammonia to produce a dark blue solution.



Qualitative Analysis Test for Fe²⁺(aq) – Addition of NH₃(aq)





Qualitative Analysis Test for Fe²⁺(aq) – Addition of NH₃(aq)









The green precipitate of $Fe(OH)_2$ is insoluble in excess aqueous ammonia.



Qualitative Analysis Test for Fe²⁺(aq) – Addition of NH₃(aq)



Note: Iron(II) can oxidise to iron(III) upon exposure to atmospheric oxygen.

When this happens, the green precipitate of $Fe(OH)_2$ changes into a red-brown precipitate of $Fe(OH)_3$.



Qualitative Analysis Test for Fe³⁺(aq) – Addition of NH₃(aq)





Qualitative Analysis Test for Fe³⁺(aq) – Addition of NH₃(aq)











The red-brown precipitate of $Fe(OH)_3$ is insoluble in excess aqueous ammonia.



Qualitative Analysis Test for Pb²⁺(aq) – Addition of NH₃(aq)





Qualitative Analysis Test for Pb²⁺(aq) – Addition of NH₃(aq)



Lead(II) Nitrate + Aqueous Ammonia \rightarrow Lead(II) Hydroxide + Ammonium Nitrate Pb(NO₃)₂(aq) + 2NH₄OH(aq) \rightarrow Pb(OH)₂(s) + 2NH₄NO₃(aq) Pb²⁺(aq) + 2OH⁻(aq) \rightarrow Pb(OH)₂(s)






The white precipitate of Pb(OH)₂ is insoluble in excess aqueous ammonia.



Qualitative Analysis Test for Zn²⁺(aq) – Addition of NH₃(aq)





Qualitative Analysis Test for Zn²⁺(aq) – Addition of NH₃(aq)









The white precipitate of Zn(OH)₂ dissolves in excess aqueous ammonia to produce a colourless solution.





Summary – Test for Cations Using Aqueous Ammonia

Cation	Effect of Aqueous Ammonia	
Aluminium cation – Al ³⁺ (aq)	White ppt., insoluble in excess.	
Ammonium cation – NH ₄ +(aq)	Not applicable.	
Calcium cation – Ca ²⁺ (aq)	No observed reaction, no ppt. observed.	
Copper(II) cation – Cu ²⁺ (aq)	Light blue ppt., soluble in excess giving a dark blue solution.	
Iron(II) cation – Fe ²⁺ (aq)	Green ppt., insoluble in excess.	
Iron(III) cation – Fe ³⁺ (aq)	Red-brown ppt., insoluble in excess.	
Lead(II) cation – Pb ²⁺ (aq)	White ppt., insoluble in excess.	
Zinc cation – Zn ²⁺ (aq)	White ppt., soluble in excess giving a colourless solution.	



Summary – Test for Cations Using Aqueous Ammonia

"Chunk" your thinking to help you remember:

• *Cu*²⁺(*aq*), *Fe*²⁺(*aq*) and *Fe*³⁺(*aq*) form *coloured precipitates* which are *insoluble* in excess aqueous ammonia. **Note:** *copper* and *iron* are both *transition metals*.

- *Al*³⁺(*aq*) and *Pb*²⁺(*aq*) form *white precipitates* which are *insoluble* in excess aqueous ammonia.
 - Ca²⁺(aq) is not seen to react with either aqueous ammonia or excess aqueous ammonia, *i.e.* no precipitate is formed.

• *Zn*²⁺(*aq*) forms a *white precipitate* which *dissolves* in excess aqueous ammonia to form a *colourless solution*.





Summary – Test for Cations Using Aqueous Ammonia



Summary – Test for Cations Using NaOH(aq) and NH₃(aq)

Cation	Effect of Aqueous Sodium Hydroxide	Effect of Aqueous Ammonia	
Aluminium cation – Al ³⁺ (aq)	White ppt., soluble in excess giving a colourless solution.	White ppt., insoluble in excess.	
Ammonium cation – $NH_4^+(aq)$	Ammonia produced on warming.	Not applicable.	
Calcium cation – Ca ²⁺ (aq)	White ppt., insoluble in excess.	No observed reaction, no ppt. observed.	
Copper(II) cation – Cu ²⁺ (aq)	Light blue ppt., insoluble in excess.	Light blue ppt., soluble in excess giving a dark blue solution.	
Iron(II) cation – Fe ²⁺ (aq)	Green ppt., insoluble in excess.	Green ppt., insoluble in excess.	
Iron(III) cation – Fe ³⁺ (aq)	Red-brown ppt., insoluble in excess.	Red-brown ppt., insoluble in excess.	
Lead(II) cation – Pb ²⁺ (aq)	White ppt., soluble in excess giving a colourless solution.	White ppt., insoluble in excess.	
Zinc cation – Zn ²⁺ (aq)	White ppt., soluble in excess giving a colourless solution.	White ppt., soluble in excess giving a colourless solution.	



Summary – Test for Cations Using NaOH(aq) and NH₃(aq)



• Click on the diagram above to view an enlarged copy.



Do not forget the qualitative tests for the H⁺(aq) cation in an acidic solution!



- Blue litmus paper turning red is not considered as a chemical test for the H⁺(aq) cation.
- Universal indicator solution turning from green to red or orange or yellow *is not* considered as a chemical test for the H⁺(aq) cation.



Adding a reactive metal, *e.g.* magnesium or zinc, to the acid, observing effervescence, and then testing the gas with a burning splint (it should be extinguished with a "pop" sound) *is* considered as a chemical test for the H⁺(aq) cation.

acid + metal \rightarrow salt + hydrogen nitric acid + zinc \rightarrow zinc nitrate + hydrogen

 $2HNO_3(aq) + Zn(s) \rightarrow Zn(NO_3)_2(aq) + H_2(g)$

 $2H^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + H_2(g)$



 Adding a carbonate, *e.g.* sodium carbonate, to the acid, observing effervescence, and then testing the gas with limewater (a white precipitate should be produced) is considered as a chemical test for the H⁺(aq) cation.

acid + carbonate \rightarrow salt + water + carbon dioxide sulfuric acid + sodium carbonate sodium sulfate + water + carbon dioxide $H_2SO_4(aq) + Na_2CO_3(aq)$ $Na_2SO_4(aq) + H_2O(l) + CO_2(g)$ $2H^+(aq) + CO_3^{2-}(aq) \rightarrow H_2O(l) + CO_2(q)$



What other qualitative tests for cations are there?

 It is possible to identify some metal cations by performing a *flame test*.









Copper Lithium (green) (red) Calcium (brick red) Sodium (orange)

Barium Pota (apple (I green)

Potassium (lilac)





During a flame test, a sample of an unknown salt (ionic compound) is heated in a non-luminous Bunsen burner flame.
Electrons in the metal cation *absorb heat energy* from the flame and are *excited* into higher energy electron shells.





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When the excited electrons *relax* back to their original electron shells (ground state) they *release energy* in the form of *visible light*. Each metal cation, with its own unique electronic configuration, produces light of different wavelengths (colours).





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Qualitative Analysis The Visible Spectrum



• The wavelength (colour) of light emitted by the metal cation is inversely proportional to the change in energy as the electron moves between electron shells.



 $E \propto \frac{I}{\lambda}$ E = energy / J and λ = wavelength / nm

Qualitative Analysis The Visible Spectrum



- The electrons in a calcium ion, Ca²⁺, which produces a red flame colour of wavelength 650 nm, undergo relatively low energy transitions when heated.
- The electrons in a potassium ion, K⁺, which produces a lilac flame colour of wavelength 400 nm, undergo relatively high energy transitions when heated.









THE COLOR OF A METEOR DEPENDS ON ITS CHEMICAL COMPOSITION

Iron

Nitrogen/Oxygen

Calcium

Sodium

Magnesium



RED STRONTIUM COMPOUNDS

WHITE BURNING MAGNESIUM, ALUMINUM OR TITANIUM



BLUE COPPER COMPOUNDS

Qualitative Analysis

ORANGE CALCIUM COMPOUNDS

SILVER SUPERHEATED MAGNESIUM OR ALUMINUM

YELLOW -SODIUM COMPOUNDS -CALCIUM + BARIUM

VIOLET

GREEN

BORON COMPOUNDS

BARIUM OR

STRONTIUM + COPPER



CARLS HIGH

Compound Interest
www.compoundchem.com

How else can heating a chemical help me to determine its composition?





 Many metal carbonates decompose on heating to produce the metal oxide and carbon dioxide gas.





 Carbon dioxide gas produces a white precipitate of calcium carbonate when bubbled through limewater:

 $Ca(OH)_{2}(aq) + CO_{2}(g)$ \downarrow $CaCO_{3}(s) + H_{2}O(l)$





• The more reactive the metal, the more stable its carbonate, and the less likely it is to undergo thermal decomposition.



Reactivity	Element	Thermal Stability of CO ₃ ^{2–}	Thermal Stability of NO ₃ ⁻
Most Reactive	Potassium – K	\downarrow	
\downarrow	Sodium – Na	↓ Me	\downarrow
\downarrow	Calcium – Ca	tal carbonates becc and decompose m → on heatir	fetal nitrates becom and decompose m → on heatir
\downarrow	Magnesium – Mg		
\downarrow	Aluminium – Al		
\downarrow	(Carbon – C)		
\downarrow	Zinc – Zn		
\downarrow	Iron – Fe	ome ore	ne le iore ⊣g –
\downarrow	Lead – Pb	less stable readily →	ess stable → readily →
\downarrow	(Hydrogen – H)		
\downarrow	Copper – Cu		
Least Reactive	Silver – Ag	\downarrow	•



- With the exception of lithium carbonate, Li₂CO₃, Group 1 metal carbonates do not decompose on heating in a non-luminous Bunsen burner flame. Note that lithium is the least reactive of the Group 1 metals.
- Carbonates of other metals (including lithium carbonate) decompose on heating in a non-luminous Bunsen burner flame to produce a metal oxide and carbon dioxide gas as the products. In general, the temperature at which metal carbonates decompose decreases upon descending the reactivity series of metals.



 Calcium carbonate (white) decomposes into calcium oxide (white) and carbon dioxide at 890 °C.
CaCO₃(s) → CaO(s) + CO₂(g)

 Zinc carbonate (white) decomposes into zinc oxide (yellow when hot, white when cold) and carbon dioxide at 400 °C.
ZnCO₃(s) → ZnO(s) + CO₂(g)

 Lead(II) carbonate (white) decomposes into lead(II) oxide (yellow) and carbon dioxide at 350 °C.
PbCO₃(s) → PbO(s) + CO₂(g)




Reversible
Decomposition
of Zinc Oxide

Zinc oxide is white when cold, but yellow when hot. When heated, the white zinc oxide loses oxygen to form a yellow non-stoichiometric* oxide. On cooling, the compound absorbs oxygen from the atmosphere to form white zinc oxide once again.
*A compound whose proportions cannot be written using integers.



Reversible
Decomposition
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Zinc oxide is white when cold, but yellow when hot. When heated, the white zinc oxide loses oxygen to form a yellow non-stoichiometric* oxide. On cooling, the compound absorbs oxygen from the atmosphere to form white zinc oxide once again.
*A compound whose proportions cannot be written using integers.

Copper(II) carbonate (green) decomposes into copper(II) oxide (black) and carbon dioxide at 300 °C.
CuCO₃(s) → CuO(s) + CO₂(g)

 Silver carbonate (yellow) decomposes into silver oxide (black) and carbon dioxide at 210 °C.
Ag₂CO₃(s) → Ag₂O(s) + CO₂(g)

The silver oxide (black) undergoes further thermal decomposition at 280 °C to form elemental silver and oxygen. $2Ag_2O(s) \rightarrow 4Ag(s) + O_2(g)$





 Thermal Decomposition of Copper(II) Carbonate

When heated by a non-luminous Bunsen burner flame, green copper(II) carbonate decomposes to form black copper(II) oxide and carbon dioxide gas. The carbon dioxide gas produces a white precipitate when bubbled through limewater.



Thermal
Decomposition
of Copper(II)
Carbonate

When heated by a non-luminous Bunsen burner flame, green copper(II) carbonate decomposes to form black copper(II) oxide and carbon dioxide gas. The carbon dioxide gas produces a white precipitate when bubbled through limewater.



Thermal
Decomposition
of Copper(II)
Carbonate

When heated by a non-luminous Bunsen burner flame, green copper(II) carbonate decomposes to form black copper(II) oxide and carbon dioxide gas. The carbon dioxide gas produces a white precipitate when bubbled through limewater.

With the exception of lithium nitrate, most Group I metal nitrates decompose on heating in a non-luminous Bunsen burner flame to produce the metal *nitrite* and oxygen gas only.
2NaNO₃(s) → 2NaNO₂(s) + O₂(g)

 Most other metal nitrates (including lithium nitrate) decompose on heating in a non-luminous Bunsen burner flame to produce the metal oxide, reddish-brown nitrogen dioxide gas (acidic) and oxygen gas (relights a glowing splint).

 $2Mg(NO_3)_2(s) \rightarrow 2MgO(s) + 4NO_2(g) + O_2(g)$





 Thermal Decomposition of Copper(II) Nitrate

> Copper(II) nitrate decomposes on heating in a non-luminous Bunsen burner flame:



 $2Cu(NO_3)_2(s) \rightarrow 2CuO(s) + 4NO_2(g) + O_2(g)$



Thermal
Decomposition
of Copper(II)
Nitrate

 The reddish-brown nitrogen dioxide gas is acidic and turns damp blue litmus paper red.



 $2Cu(NO_3)_2(s) \rightarrow 2CuO(s) + 4NO_2(g) + O_2(g)$





 Oxygen gas supports combustion and relights a glowing splint.



 $2Cu(NO_3)_2(s) \rightarrow 2CuO(s) + 4NO_2(g) + O_2(g)$

Lead(II) nitrate decompose into lead(II) oxide, nitrogen dioxide and oxygen. The decomposition is accompanied by a loud cracking sound called *decrepitation*.
2Pb(NO₃)₂(s) → 2PbO(s) + 4NO₂(g) + O₂(g)

 Silver nitrate starts to decompose into silver, nitrogen dioxide and oxygen at 250°C, and decomposes completely at 440°C.

 $2AgNO_3(s) \rightarrow 2Ag(s) + 2NO_2(g) + O_2(g)$



Can I please have some questions to check my understanding?







Qualitative Analysis The Reactions

Formation of blue precipitate R: $Cu^{2+}(aq) + 2OH^{-}(aq) \rightarrow Cu(OH)_{2}(s)$

Formation of solution **T** and solid **U**: $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$

Formation of white precipitate **W**: $Zn^{2+}(aq) + 2OH^{-}(aq) \rightarrow Zn(OH)_{2}(s)$











Qualitative Analysis The Reactions

Formation of gas L and solution M: $Ca(s) + 2HCl(aq) \rightarrow CaCl_{2}(aq) + H_{2}(g)$ ionic equation: $Ca(s) + 2H^{+}(aq) \rightarrow Ca^{2+}(aq) + H_{2}(g)$ Formation of white precipitate N: $CaCl_{2}(aq) + 2NaOH(aq) \rightarrow Ca(OH)_{2}(s) + 2NaCl(aq)$ ionic equation: $Ca^{2+}(aq) + 2OH^{-}(aq) \rightarrow Ca(OH)_{2}(s)$







Reddish-brown precipitate E – Fe(OH)₃(s).

THAN YANG

Qualitative Analysis The Reactions

Formation of gas **B** and solution **C**: $FeCO_3(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2O(l) + CO_2(g)$ ionic equation: $FeCO_3(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2O(l) + CO_2(g)$



Qualitative Analysis The Reactions

Formation of green precipitate **D**: with aqueous sodium hydroxide: $FeCl_2(aq) + 2NaOH(aq) \rightarrow Fe(OH)_2(s) + 2NaCl(aq)$ ionic equation $Fe^{2+}(aq) + 2OH^{-}(aq) \rightarrow Fe(OH)_{2}(s)$ Formation of green precipitate **D**: with aqueous ammonia: $FeCl_2(aq) + 2NH_4OH(aq) \rightarrow Fe(OH)_2(s) + 2NH_4Cl(aq)$ ionic equation $Fe^{2+}(aq) + 2OH^{-}(aq) \rightarrow Fe(OH)_{2}(s)$



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