Why does flame change colour:

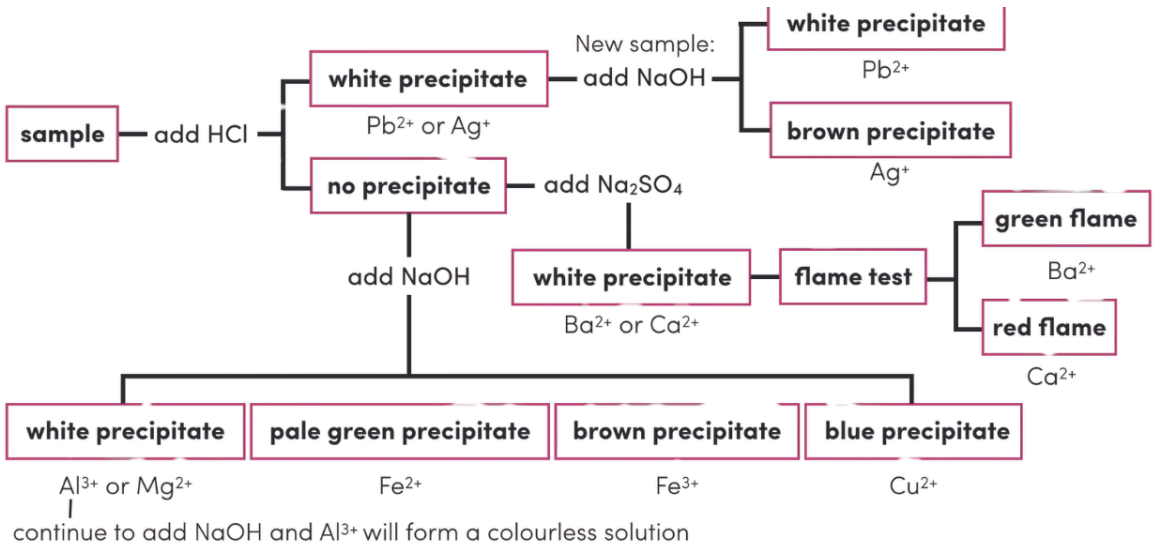
Electrons absorb heat energy which excites them so that they jump to a higher energy level (electron in an 'excited state'). Electrons return to their ground state and emit excess energy in the form of light (emitted energy = higher energy - lower energy)

Positive Flame Test Results

METAL CATION	COLOUR	METAL CATION	COLOUR
Barium (Ba^{2+})	Green	Iron(III) (Fe^{3+})	Sparkly gold
Calcium (Ca^{2+})	Red	Potassium (K^{+})	Lilac
Magnesium (Mg^{2+})	Bright white	Sodium (Na^{+})	Yellow
Copper(II) (Cu^{2+})	Blue/green	Lithium (Li^{+})	Red
Iron(II) (Fe^{2+})	Sparkly gold	Strontium (Sr^{2+})	Scarlet

Limitations of flame test:

1. Some metals don't produce colours
2. Some metals are unsafe to test (for example lead which produces toxic fumes when burnt) - solutions: use percipitation or AAS tests to identify lead in a sample
3. Difficult to differentiate between ions with the same or similar colour: Calcium, lithium and Stronium all produce reddish flames



For Anions: Use the KISS table. However, the second table has a test for nitrate.

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A Simple Scheme for Identifying Anions

Solution Containing One Anion:

Cl^- Br^- I^- OH^- CH_3COO^- CO_3^{2-} SO_4^{2-} PO_4^{3-}

CH_3COO^- ???
This ion derives from ethanoic acid and is also known as "ethanoate" ion.

Step 1. Add Acid

- Gas Bubbles Form (CO_2 gas) → **CO_3^{2-}**
  Can check this by adding Ca^{2+} ions to a fresh sample. Carbonate ion will form a heavy white pptte of $CaCO_3$.
- No Bubbles

Step 2. (with fresh sample) Add $Fe^{3+}_{(aq)}$

- No Reaction (or any other colour pptte)
- Pink Precipitate → **PO_4^{3-}**
- Brown Precipitate → **OH^-**

Confirm PO_4^{3-} with a complexation test.

Step 3. (with fresh sample) Add $Ba^{2+}_{(aq)}$

- Thick White Precipitate → **SO_4^{2-}**
- No Reaction (or only faint pptte)

Step 4. (with fresh sample) Add $Ag^+_{(aq)}$

- No Reaction
- White Precipitate → **Cl^-**
- Cream Colour Precipitate → **Br^-**
- Yellow Precipitate → **I^-**

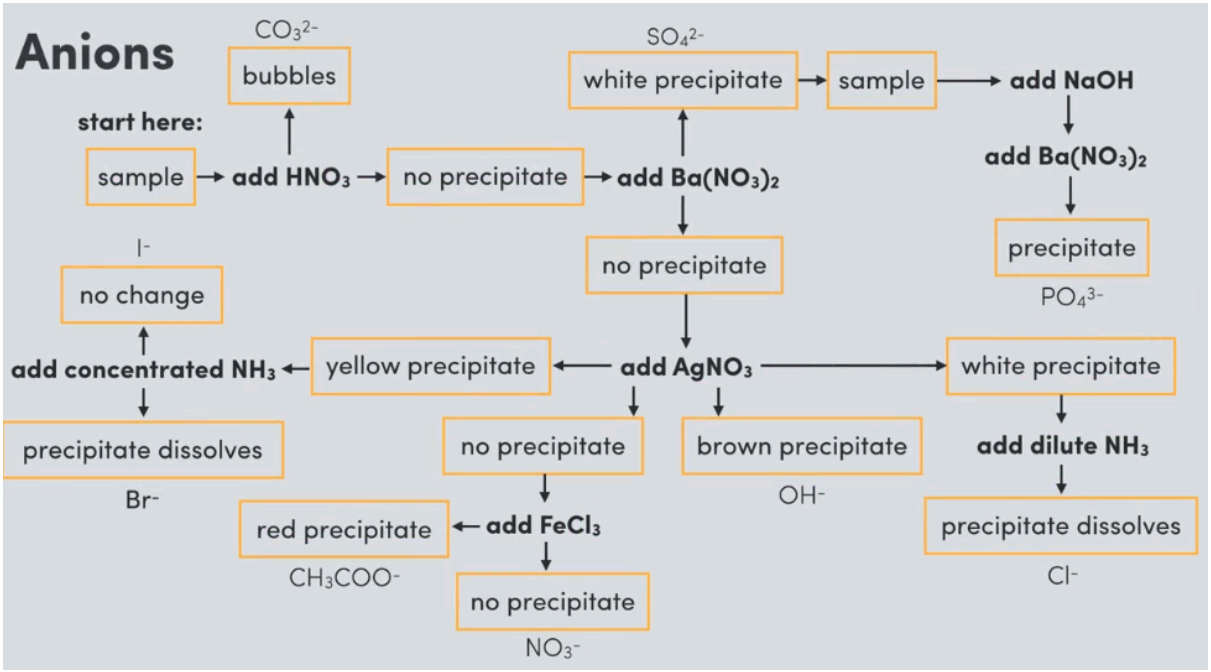
Step 5.
By elimination, the anion must be

CH_3COO^- **(of those in our hit-list.)**

To confirm this, take a fresh sample in a test tube. Add an equal volume of dilute acid and warm gently.

Carefully (by wafting air) check for the smell of vinegar.
(In acid solution, acetate ions form acetic (ethanoic) acid which evaporates when warmed, This is, of course, the acid in vinegar which gives the characteristic odour)

These colour differences may be influenced by concentration, so a complexation reaction may be used to confirm these.
a) Divide the pptte into 2 parts.
b) Add (drop by drop) dilute ammonia soln. (NH_4OH soln.)
If pptte re-dissolves, the anion present is chloride.
c) If not re-dissolved, use the 2nd sample and add (drop-wise) concentrated NH_4OH soln. DANGER! Fume cupboard job!
d) If pptte re-dissolves, the anion present is bromide.
If pptte does NOT re-dissolve, the anion present is iodide.
(Complexation reaction explained later)



Complexation

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Selected Complexation Tests

A "co-ordination complex" (or "metal complex") is a chemical compound or ion formed when a central metal atom becomes surrounded by, and bonded to, a number of molecules or ions. The surrounding molecules or ions are called "ligands" and may include polyatomic ions.

The "transition metals" (d-block of Periodic Table) often form complexes which have bright & characteristic colours. These complexes have long been used to make pigments for colouring fabrics, paints, etc. They are also very useful for chemical identification...

Identifying Silver or Lead Ions

Silver ions form a white precipitate with Cl^- ions.

$$Ag^+_{(aq)} + Cl^-_{(aq)} \longrightarrow AgCl_{(s)}$$

To verify that the precipitate IS AgCl (and not $PbCl_2$) carry out the precipitation in a test tube, then:

1. Add a few drops of dilute nitric acid to the pptte.
2. Now add (drop-wise) dilute ammonia solution. (This is the same as ammonium hydroxide soln.)

Solid silver chloride will re-dissolve as it forms a soluble complex ion:

$$AgCl_{(s)} + 2NH_{3(aq)} \longrightarrow [Ag(NH_3)_2]^+_{(aq)} + Cl^-_{(aq)}$$

diaminesilver complex ion

Lead chloride does NOT re-dissolve in ammonia.

To verify suspected Pb^{2+} ions use another similar complexation reaction:

1. Take a fresh sample of the "unknown". Add NaOH solution. This produces a pptte of $Pb(OH)_{2(s)}$.

$$Pb^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Pb(OH)_{2(s)}$$

2. Continue adding NaOH solution. Lead(II) hydroxide will re-dissolve as it forms a soluble complex ion:

$$Pb(OH)_{2(s)} + 2OH^- \longrightarrow [Pb(OH)_4]^{2-}_{(aq)}$$

Phosphate Ion Test

Phosphate ions can be positively identified as follows:

- In a test tube, add a few drops of nitric acid to your "unknown". Then add ammonium molybdate solution and heat gently in a bunsen flame.
- If phosphate ions are present a bright yellow precipitate will form.

Explanation:
Ammonium molybdate is a "metal complex" around an atom of the element molybdenum (atomic No. 42). Formula is $(NH_4)_2MoO_4$.

The yellow pptte is an even more complicated complex called ammonium phosphomolybdate.
(The KISS Principle prevents us from going there!)

Identifying Iron Ions

Ferrous ions (Fe^{2+}) and ferric ions (Fe^{3+}) can be difficult to tell apart. This may be due to the rapid oxidation of Fe^{2+} to Fe^{3+} when solutions are exposed to air. This means that solutions containing ferrous ions soon contain ferric ions as well.

A definitive test for Fe^{3+} ions involves the formation of a complex ion with an intense red colour often described as "dragon's blood".

- Add a few drops of ammonium thiocyanate (NH_4CNS) to a fresh sample of your "unknown".

$$Fe^{3+}_{(aq)} + CNS^-_{(aq)} \longrightarrow [Fe(CNS)]^{2+}_{(aq)}$$

thiocyanate ion → ferric thiocyanate complex ion

The bright red complex is soluble.

- The ferrous ion will NOT react. However, because it rapidly oxidises to ferric ion, you may get a pale-red colour in your test tube.
- There is another complexation test which is specific for ferrous ions. We leave it to your teacher, or your own research, to find it.

(The KISS Principle demands that we are NOT the ones to cause any confusion!)

Chloride, Bromide & Iodide Ions

All 3 of these will form a pptte with Ag^+ ions:

$$Ag^+_{(aq)} + Cl^-_{(aq)} \longrightarrow AgCl_{(s)}$$
$$Ag^+_{(aq)} + Br^-_{(aq)} \longrightarrow AgBr_{(s)}$$
$$Ag^+_{(aq)} + I^-_{(aq)} \longrightarrow AgI_{(s)}$$

Using "X" to stand for any halide (group 7) element, these can all be described as "AgX".

Furthermore, if the precipitate is treated with ammonia (NH_3) the same complex ion is formed around the silver ion:

$$AgX_{(s)} + 2NH_{3(aq)} \longrightarrow [Ag(NH_3)_2]^+ + X^-$$

silver halide + ammonia → diaminesilver complex ion + halide ion

The difference is that the:
- chloride version is soluble, so the pptte re-dissolves.
- bromide version is "sparingly soluble" so it re-dissolves only if treated with concentrated NH_3.
- iodide version is highly insoluble. The pptte does not re-dissolve.

Now Try Worksheets 1 & 2