

# LABORATORY 1

## CATIONS AND ANIONS IDENTIFICATION AS AN EXAMPLE OF CHEMICAL ANALYSIS

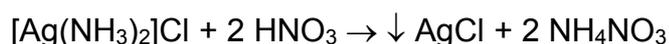
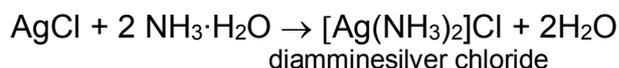
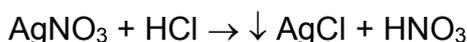
### CATIONS

#### Silver ion ( $\text{Ag}^+$ )

Silver is a metal element, which exists in compounds as monovalent cation. Although many silver salts are sparingly soluble, silver nitrate is easily soluble in water. Silver nitrate is used in medicine in dermatologists practice as a lunar caustic (lapis).

#### Detection of $\text{Ag}^+$

Hydrochloric acid or soluble chlorides precipitate white silver chloride sediment from solutions containing soluble silver salts (e.g. silver nitrate). Silver chloride can be solubilized in ammonia solution ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ), yielding complex compound -  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ , diamminesilver chloride.  $\text{AgCl}$  precipitate can be obtained again on addition of nitric acid to the solution.



**Procedure:** Add 5 drops of silver salt ( $\text{Ag}^+$ ) solution to a test tube and then add 2 drops of 2M HCl. Observe formation of  $\text{AgCl}$  white precipitate. Add water solution of ammonia ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ) in excess and mix. The precipitate will dissolve. Add some drops of  $\text{HNO}_3$  to the solution -  $\text{AgCl}$  precipitate will be formed again.

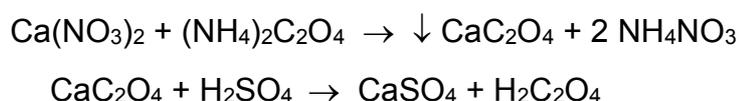
#### Calcium ion ( $\text{Ca}^{2+}$ )

Calcium cation, present like barium in the second group of elements in the periodic table, forms bivalent ions. Calcium compounds are commonly found in nature as minerals, mostly in forms of calcium carbonate  $\text{CaCO}_3$  (chalk), hydrated calcium sulphate  $\text{CaSO}_4 \times 2 \text{H}_2\text{O}$  (gypsum) and

semihydrate calcium sulphate  $2 \text{CaSO}_4 \times \text{H}_2\text{O}$  (used as surgical plaster of Paris). Calcium phosphate  $\text{Ca}_3(\text{PO}_4)_2$  forms a main stiff structural compound of bone. Calcium ions play important roles in metabolic processes. These include: activation of enzymes, increase of the contractility of myofibrils, participation in blood coagulation process.

### **Detection of $\text{Ca}^{2+}$**

1. Ammonium oxalate  $((\text{NH}_4)_2\text{C}_2\text{O}_4)$  forms calcium oxalate  $(\text{CaC}_2\text{O}_4)$  sediment with soluble calcium salts. The sediment can be easily solubilized in mineral acids. This reaction is applied for quantitative analysis of  $\text{Ca}^{2+}$  ions.



**Procedure:** Add 2 drops of ammonium oxalate  $((\text{NH}_4)_2\text{C}_2\text{O}_4)$  to some drops of calcium salt  $(\text{Ca}^{2+})$  solution and observe formation of a white calcium oxalate  $(\text{CaC}_2\text{O}_4)$  sediment. Solubilize the sediment with a few drops of 1M sulfuric acid  $(\text{H}_2\text{SO}_4)$  solution.

2. While heating the platinum wire with calcium salt solution in a flame, as the result of calcium electrons excitation, change the flame color to reddish-brown is observed.

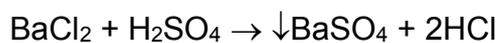
**Procedure:** Anneal the platinum wire in the laboratory burner flame until the flame becomes colorless. Then immerse the wire in calcium salt  $(\text{Ca}^{2+})$  solution and put it back to the flame again. Observe the change of color flame to reddish-brown.

## **Barium ion ( $\text{Ba}^{2+}$ )**

Barium is a heavy metal which forms bivalent compounds. All water-soluble barium salts are toxic. Barium sulfate is not toxic, it is sparingly soluble in water, acids and bases. Barium sulfate strongly absorbs the X-ray radiation and is used in medical examination as a contrasting agent in roentgenoscopy.

### **Detection of $\text{Ba}^{2+}$**

1. Sulfuric acid and its soluble salts form abundant white sediment of barium sulfate after mixing with barium cations containing solutions.



**Procedure:** Add 2 drops of 1M sulfuric acid to 5 drops of barium salt ( $\text{Ba}^{2+}$ ) solution and observe precipitation of barium sulfate. Check insolubility of barium sulfate with solutions of strong acid (2M HCl) and strong base (2M NaOH).

2. While heating the platinum wire with barium salt ( $\text{Ba}^{2+}$ ) solution in a flame, as the result of barium electrons excitation, change the flame color to green is observed.

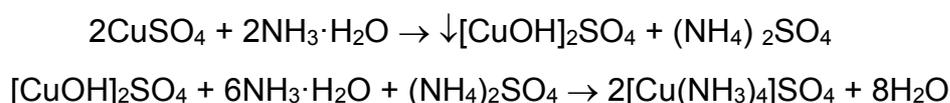
**Procedure:** Anneal the platinum wire in the laboratory burner flame until the flame becomes colorless. Then, dip the wire into the barium salt solution and put it back into the flame. Observe a green color of the flame.

## Copper ion ( $\text{Cu}^{2+}$ )

Copper ion is a microelement, and is necessary to activate the reserves of  $\text{Fe}^{2+}$  for hemoglobin biosynthesis. Copper is present in the blood, bound to the glycoprotein called ceruloplasmin.

### **Detection of $\text{Cu}^{2+}$**

Ammonia from water solution ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ) precipitates white-bluish, basic copper sulfate from copper cations solution. After adding ammonia in excess, the solution clarifies and the color changes to dark blue, signaling formation of complex salt  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  (tetraamminecopper (II) sulphate).



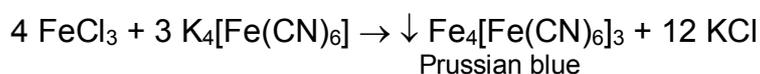
**Procedure:** Add one drop of 2M  $\text{NH}_3 \cdot \text{H}_2\text{O}$  to 5 drops of copper ( $\text{Cu}^{2+}$ ) salt solution. The precipitate of white-bluish basic salt ( $[\text{CuOH}]_2\text{SO}_4$ ) is formed. Add an excess of ammonia (several drops) - dark-blue color product – a tetraamminecopper (II) sulphate ( $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ ) is formed.

## Ferric (Fe<sup>3+</sup>) and ferrous (Fe<sup>2+</sup>) ions

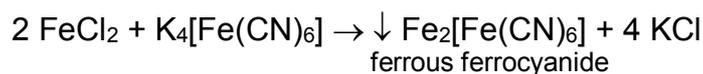
There are generally bi- and trivalent ions of iron, found in nature and human body. Ferrous (Fe<sup>2+</sup>) ions can be easily oxidized to ferric ions (Fe<sup>3+</sup>) in an open air. Ferrous ions are absorbed in digestive tract and are present in hemoglobin and myoglobin, however ferric ions are transported in blood and stored. Ferrous and ferric ions form oxido-reducing pair in cytochrome molecules in the respiratory system of mitochondria.

### Detection of iron ions Fe<sup>3+</sup> and Fe<sup>2+</sup>

1. Potassium ferrocyanide [hexacyanoferrate (II)] - K<sub>4</sub>[Fe(CN)<sub>6</sub>] forms with ferric ions (Fe<sup>3+</sup>) a dark-blue precipitate of ferric ferrocyanide (Prussian blue) - Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub>.



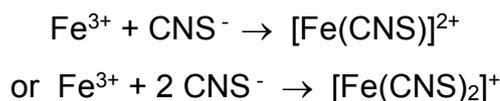
With the same reagent, the ferrous ions (Fe<sup>2+</sup>) form a light blue sediment of ferrous ferrocyanide.



The product in an open test tube is easily oxidized with air oxygen to ferric ferrocyanide (Prussian blue).

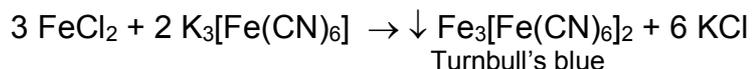
**Procedure:** Add a few drops of potassium ferrocyanide (K<sub>4</sub>[Fe(CN)<sub>6</sub>]) to 5 drops of Fe<sup>3+</sup> solution and observe formation of dark-blue precipitate of ferric ferrocyanide (Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub>).

2. Ammonium thiocyanate (rhodanate) (CNS<sup>-</sup> anion) reacts with ferric ions Fe<sup>3+</sup>, forming intense blood-red color complex compound ("dragon's blood"). This is the most characteristic reaction used for detection of Fe<sup>3+</sup> ions. Because of easy oxidation of Fe<sup>2+</sup> ions to Fe<sup>3+</sup> in open air test tube, light red color can also be formed with ferrous ion test solution.



**Procedure:** Add a few drops of ammonium thiocyanate (NH<sub>4</sub>CNS) to some drops of Fe<sup>3+</sup> ions solution and mix. A red color complex compound forms.

3. When potassium ferricyanide  $K_3[Fe(CN)_6]$  [hexacyanoferrate (III)] is added to ferrous  $Fe^{2+}$  ions solution, the blue precipitate of ferrous ferricyanide (Turnbull's blue) -  $Fe_3[Fe(CN)_6]_2$  is formed. This is a specific reaction used for  $Fe^{2+}$  ions detection.



**Procedure:** Add 2 drops of potassium ferricyanide solution ( $K_3[Fe(CN)_6]$ ) to some drops of  $Fe^{2+}$  solution to obtain Turnbull's blue ( $Fe_3[Fe(CN)_6]_2$ ) precipitate.

## Sodium ion ( $Na^+$ )

Sodium is a human body extracellular element. It is commonly present in living organisms and in various minerals as monovalent ion.

Almost all sodium salts are easily soluble in water. Sodium ion can be easily excited in the temperature of laboratory burner flame, resulting in visible strong yellow light emission. It does not form characteristic insoluble salt sediments, so it can be identified and quantitatively measured using a flame test.

### Detection of $Na^+$

**Procedure:** Anneal the platinum wire in the laboratory burner flame until the flame becomes colorless. Next dip the wire into the sodium salt ( $Na^+$ ) solution and put it back to the flame. Observe the change of the flame color to strong yellow.

## Potassium ion ( $K^+$ )

Potassium is human body intracellular element. It is commonly present in living organisms and in various minerals as monovalent ion.

### Detection of $K^+$

**Procedure:** Anneal the platinum wire in the laboratory burner flame until the flame becomes colorless. Next dip the wire into the potassium salt ( $K^+$ ) solution and put it back to the flame. Observe the change of the flame color to violet.

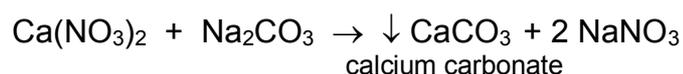
## ANIONS

### Carbonate ion ( $\text{CO}_3^{2-}$ )

Carbonic acid  $\text{H}_2\text{CO}_3$  is a very weak electrolyte, with two steps dissociation reaction. One proton dissociation of carbonic acid takes place in neutral pH solutions and leads to formation of bicarbonate anion  $\text{HCO}_3^-$ . The presence of this ion in blood is very important and, together with blood-solubilized carbon dioxide, forms a principal blood pH buffering system. Dissociation of second proton needs slightly basic media and leads to formation of carbonate ions  $\text{CO}_3^{2-}$ .

#### Detection of $\text{CO}_3^{2-}$

1. Calcium nitrate precipitates white sediment of calcium carbonate from carbonic ions solutions.



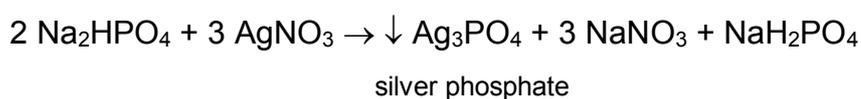
**Procedure:** Add a few drops of calcium nitrate ( $\text{Ca}(\text{NO}_3)_2$ ) solution to 5 drops of carbonate ions ( $\text{CO}_3^{2-}$ ) solution to obtain a white sediment of calcium carbonate.

### Phosphate ion ( $\text{PO}_4^{3-}$ )

Calcium phosphate  $\text{Ca}_3(\text{PO}_4)_2$  is dominant in nature, a water-insoluble phosphate salt, found also in vertebrates in bones. Phosphate ions ( $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ) are commonly present in intercellular medium and organic natural compounds, phosphate esters play a very important role in biology of living matter. Anhydride bindings between ortho-phosphoric acid molecules form chemical energy storage molecules (ATP). A mixture of phosphate ions forms pH stabilizing system in human body fluids.

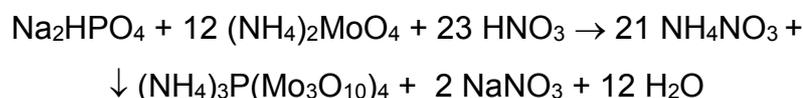
#### Detection of $\text{PO}_4^{3-}$

1. Silver phosphate is precipitated from phosphate ions solution after addition of silver nitrate solution.



**Procedure:** Add a few drops of silver nitrate (AgNO<sub>3</sub>) to 5 drops of phosphate ions (PO<sub>4</sub><sup>3-</sup>) solution. The light-yellow precipitate of silver phosphate will appear.

2. In the presence of an excess of ammonium molybdate, phosphate ions precipitate as yellow ammonium phosphomolybdate salt (V).



**Procedure:** Add 6-7 drops of molybdenic mixture to several drops of phosphate ions (PO<sub>4</sub><sup>3-</sup>) solution. Heat it slightly over a flame and observe formation of yellow precipitate of ammonium phosphomolybdate.

## Sulfate ion (SO<sub>4</sub><sup>2-</sup>)

### Detection of SO<sub>4</sub><sup>2-</sup>

Barium chloride or barium nitrate precipitates a barium sulfate sediment from sulfate ions solution. Barium sulfate is sparingly soluble in acids and bases.



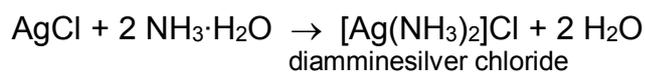
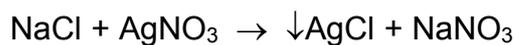
**Procedure:** Add a few drops of barium nitrate to some drops of sulfate ions (SO<sub>4</sub><sup>2-</sup>) solution and observe formation of abundant white barium sulfate sediment.

## Chloride ion (Cl<sup>-</sup>)

Chloride is very important anion, present in blood serum and in other extracellular media. Chloride ions are very common in nature and are present in tap water.

Silver nitrate (AgNO<sub>3</sub>) reacts with chloride solution to precipitate white silver chloride. Silver chloride is soluble in excess of NH<sub>3</sub>·H<sub>2</sub>O, yielding complex compound - [Ag(NH<sub>3</sub>)<sub>2</sub>]Cl, diamminesilver chloride.

## Detection of Cl<sup>-</sup>



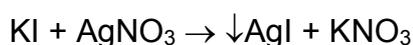
**Procedure:** Add a few drops of silver nitrate solution to a test tube containing some drops of chloride anions (Cl<sup>-</sup>) solution. As a result AgCl precipitate is formed. Add drop by drop 2M NH<sub>3</sub>·H<sub>2</sub>O solution, until the precipitate is dissolved. AgCl can be reprecipitated again upon addition of nitric acid.

## **Iodide ion ( I<sup>-</sup> )**

Iodine is another significant microelement of halogenes family. Iodide ions are absorbed by thyroid gland, oxidated to iodine and incorporated into thyroid hormones.

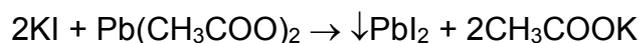
### Detection of I<sup>-</sup>

1. Silver nitrate (AgNO<sub>3</sub>) reacts with iodide ions to precipitate yellow silver iodide.



**Procedure:** Add a few drops of silver nitrate solution to some drops of iodide ions (I<sup>-</sup>) solution and observe formation of a light-yellow precipitate of silver iodide.

2. Lead acetate reacts with iodide ions and yellow precipitate of lead iodide is formed



**Procedure:** Add a few drops of Pb(CH<sub>3</sub>COO)<sub>2</sub> solution to some drops of iodide ions (I<sup>-</sup>) solution. A yellow precipitate of lead (II) iodide PbI<sub>2</sub> is formed.

**Examples of questions from a lab on a lab test # 1:**

1. How can you detect  $\text{CO}_3^{2-}$  in  $\text{Na}_2\text{CO}_3$  (sodium carbonate)? Write appropriate reaction(s).
2. How to detect both ions in  $\text{CaCl}_2$ ? Write appropriate reactions.
3. How can you differentiate  $\text{FeCl}_3$  (ferric chloride) from  $\text{FeCl}_2$  (ferrous chloride)? Write appropriate reaction(s).
4. How can you detect both ions in  $\text{NaCl}$  ?
5. How can you differentiate  $\text{NaCl}$  from  $\text{NaI}$  ?