

LABORATORY 1

CATIONS AND ANIONS IDENTIFICATION AS AN EXAMPLE OF CHEMICAL ANALYSIS

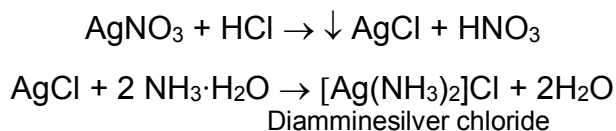
CATIONS

Silver ion (Ag⁺)

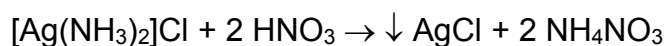
Silver is a metal element, which exists in compounds as monovalent cation. Although many silver salts are sparingly soluble, silver nitrate is easily soluble in water. Silver nitrate is used in medicine in dermatologists practice as a lunar caustic (lapis).

Detection of 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 ammonium hydroxide (NH₃·H₂O), yielding complex compound - [Ag(NH₃)₂]Cl, diamminesilver chloride.



Procedure: Add 0.5 - 1.0 ml of silver salt solution to a test tube and then add 2 drops of 2M HCl. Observe formation of AgCl white precipitate. Take a portion of the precipitate and transfer to another test tube. Add the NH₃·H₂O solution in excess. The precipitate will dissolve. AgCl precipitate can be obtained again on addition of nitric acid to the solution:



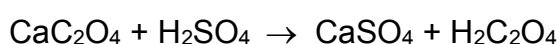
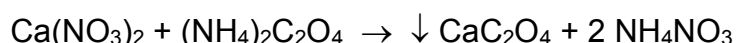
Calcium ion (Ca²⁺)

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 CaCO₃ (chalk), hydrated calcium sulphate CaSO₄ × 2 H₂O (gypsum) and semihydrate calcium sulphate 2 CaSO₄ × H₂O (used as surgical plaster of Paris). Calcium phosphate Ca₃(PO₄)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. In human organism calcium comprises 1.5% of the total body weight.

Detection of Ca²⁺

1. Ammonium oxalate $(\text{NH}_4)_2\text{C}_2\text{O}_4$ or oxalic acid $\text{H}_2\text{C}_2\text{O}_4$, from soluble calcium salts, precipitate as calcium oxalate (CaC_2O_4) sediment. The sediment can be easily solubilized in mineral acids. This reaction is applied for quantitative analysis of Ca^{2+} ions.



Procedure: Add 2 drops of ammonium oxalate $(\text{NH}_4)_2\text{C}_2\text{O}_4$ or oxalic acid $\text{H}_2\text{C}_2\text{O}_4$ to 0.5 - 1.0 ml of calcium salt solution, and observe formation of a white calcium oxalate sediment. Solubilize the sediment with a few drops of 1M sulfuric acid solution.

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

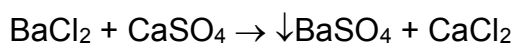
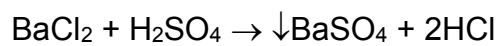
Procedure: Anneal the platinum wire in the laboratory burner flame until the flame becomes colorless. Then immerse the wire in calcium salt solution and put it back to the flame again. Observe the change of color flame to reddish-brown.

Barium ion (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 Ba²⁺

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 (or gypsum water) to 0.5-1.0 ml of barium salt solution and observe precipitation of barium sulfate. Check insolubility of barium sulfate with solutions of strong acid (HCl) and strong base (NaOH).

2. While heating the platinum wire with barium salt solution in a flame, as the result of barium ion electrons excitation, change the flame color to green is observed.

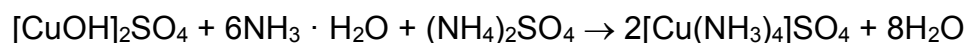
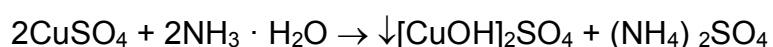
Procedure: Anneal the platinum wire in the laboratory burner flame until the flame becomes colorless. Then, dip the wire into the barium salt solution and put it back into the flame. Observe a green color of the flame.

Copper ion (Cu^{2+})

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

Detection of Cu^{2+}

Ammonium hydroxide precipitates from CuSO_4 solution white-bluish, basic copper sulfate. After adding of ammonium hydroxide 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).



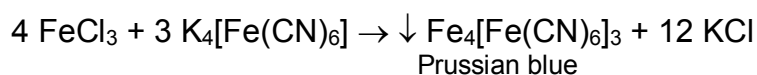
Procedure: Add a few drops of 2M NH_4OH to 1 ml of CuSO_4 solution. The precipitate is white-bluish basic salt $[\text{CuOH}]_2\text{SO}_4$ that solubilizes in an excess of ammonia, giving the dark-blue color product – a tetraamminecopper sulphate – $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$.

Ferric (Fe³⁺) and ferrous (Fe²⁺) ions

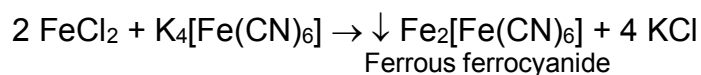
There are generally bi- and trivalent ions of iron, found in nature and human body. Ferrous (Fe²⁺) ions can be easily oxidized to ferric ions (Fe³⁺) in an open air. Ferrous ions are absorbed in digestive tract and are present in hemoglobin and myoglobin, however ferric ions are transported in blood and stored. Ferrous and ferric ions form oxido-reducing pair in cytochrome molecules in the respiratory system of mitochondria.

Detection of iron ions Fe³⁺ and Fe²⁺

1. Potassium ferrocyanide [hexacyanoferrate (II)] forms with ferric ions [Fe³⁺] a dark-blue precipitate of ferric ferrocyanide (Prussian blue).



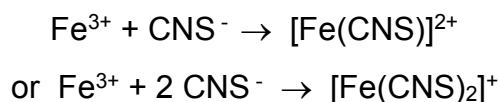
With the same reagent, the ferrous ions (Fe²⁺) form a white sediment of ferrous ferrocyanide.



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 to 0.5 – 1.0 ml of Fe³⁺ solution, and dark-blue precipitate of ferric ferrocyanide will form.

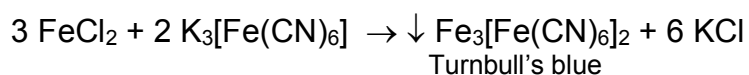
2. Ammonium thiocyanate (rhodanate) (CNS⁻ anion) reacts with ferric ions Fe³⁺, forming intense blood-red color complex compound (“dragon’s blood”). This is the most characteristic reaction used for detection of Fe³⁺ ions. Because of easy oxidation of Fe²⁺ ions to Fe³⁺ in open air test tube, light red color can also be formed with ferrous ion test solution.



Procedure: Add a few drops of ammonium thiocyanate to 0.5 - 1.0 ml of Fe³⁺ ions solution and mix. A red color-complex compound will form.

3. When potassium ferricyanide K₃[Fe(CN)₆] [hexacyanoferrate (III)] is added to ferrous Fe²⁺ ions solution, the blue precipitate of ferrous ferricyanide is formed (Turnbull’s blue). This is a specific

reaction used for Fe^{2+} ions detection. Ferric ions do not precipitate under these conditions, giving rather dark-brown color solution.



Procedure: Add 2 drops of potassium ferricyanide solution to 0.5 -1.0 ml of Fe^{2+} solution to obtain Turnbull's blue precipitate.

Sodium ion (Na^+)

Sodium is a human body extracellularly 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 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 solution and put it back to the flame. Observe the change of the flame color to violet.

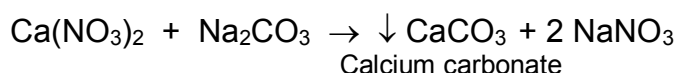
ANIONS

Carbonate ion (CO₃²⁻)

Carbonic acid H₂CO₃ 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 HCO₃⁻. 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 CO₃²⁻.

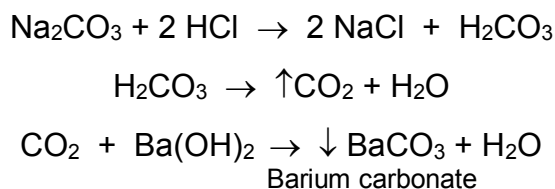
Detection of CO₃²⁻

1. Calcium nitrate or barium hydroxide precipitates from carbonic ions solutions a sediment of calcium or barium carbonate:



Procedure: Add a few drops of calcium nitrate (Ca(NO₃)₂) solution to 0.5 – 1.0 ml of carbonate ions solution to obtain a white sediment of calcium carbonate.

2. Strong acids decompose carbonate salts, releasing carbon dioxide gas, which can be detected as gas bubbles on the test tube walls, or in a form of white sediment of barium carbonate, after adding a few drops of baryta water - Ba(OH)₂.



Procedure: Add a few drops of 1M H₂SO₄ (or HCl) solution to the carbonate salt solution (0.5 - 1.0 ml) and seal the test tube using cork stopper with U-shaped glass tubing. Carefully mix the tube content and observe gas bubbles, settling on the tube walls. Quickly immerse free end of the tubing in baryta water and observe formation of barium carbonate white sediment.

Phosphate ion (PO₄³⁻)

Calcium phosphate Ca₃(PO₄)₂ is dominant in nature, a water-insoluble phosphate salt, found also in vertebrates in bones. Phosphate ions (HPO₄²⁻, H₂PO₄⁻) 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 (ATP) form chemical energy storage molecules. A mixture of phosphate ions forms pH stabilizing system in human body fluids.

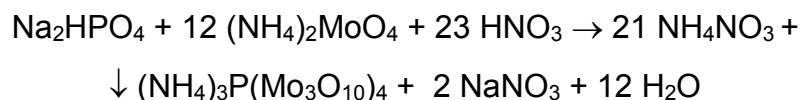
Detection of PO₄³⁻

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



Procedure: Add a few drops of silver nitrate to 0.5 - 1.0 ml of phosphate ions 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 phospho-molybdate salt (V).

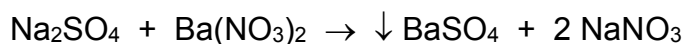


Procedure: Add 6-7 drops of molybdenic mixture and a few drops of nitric acid to 0.5 – 1.0 ml of phosphate ions solution. Heat it slightly over a flame and observe formation of yellow precipitate of ammonium phosphomolybdate.

Sulfate ion (SO₄²⁻)

Detection of SO₄²⁻

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



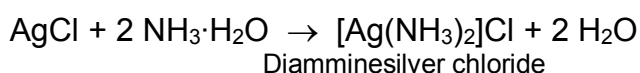
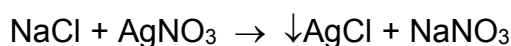
Procedure: Add a few drops of barium nitrate (chloride) to 1 ml of sulfate ions solution and observe formation of abundant white barium sulfate sediment.

Chloride ion (Cl⁻)

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 (AgNO₃) reacts with chloride solution to precipitate white silver chloride. Silver chloride is soluble in excess of NH₃·H₂O, in solutions of Na₂S₂O₃, KCN and concentrated HCl.

Detection of Cl⁻



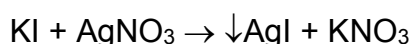
Procedure: Add a few drops of silver nitrate solution to a test tube containing 0.5 - 1.0 ml of chloride anions solution. As a result AgCl precipitate is formed. Transfer a portion of the precipitate to another test tube and add drop by drop 2M NH₃·H₂O solution, until the precipitate is dissolved. AgCl can be reprecipitated again upon addition of nitric acid.

Iodide ion (I⁻)

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

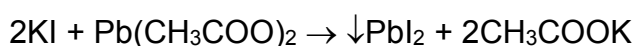
Detection of I⁻

1. Silver nitrate (AgNO₃) reacts with iodide ions to precipitate yellow silver iodide.



Procedure: Add a few drops of silver nitrate solution to 1 ml of iodide ions 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 $\text{Pb}(\text{CH}_3\text{COO})_2$ solution to 1 ml of potassium iodide solution. A yellow precipitate of lead (II) iodide PbI_2 is formed.

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

1. How can you detect CO_3^{2-} in Na_2CO_3 (sodium carbonate)? Write appropriate reaction(s).
2. How to detect both ions in CaCl_2 ? Write appropriate reactions.
3. How can you differentiate FeCl_3 (ferric chloride) from FeCl_2 (ferrous chloride) ? Write appropriate reaction(s).
4. How can you detect both ions in NaCl ?
5. How can you differentiate NaCl from NaI ?