ANALYTICAL CHEMISTRY LABORATORY MANUAL

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DECLARATION

NAME-SURNAME:

STUDENT NUMBER:

I have been informed about the safety rules in the Analytical Chemistry Laboratory by instructors. I also have been warned about the possible dangers which I meet in laboratory in case I do not obey the safety rules. I understand the importance of personal safety and know that I should wear **safety glasses, laboratory coat and gloves** for the protection at all times in the Analytical Chemistry Laboratory. I accept the full responsibilities of any possible lab accidents in case of violation of safety rules.

If I do not abide by the safety rules, I will not hold instructors of Analytical Chemistry Laboratory liable for any injuries which result.

Date:

Place: Analytical Chemistry Laboratory

Signature:

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Date:

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Signature:

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ANALYTICAL CHEMISTRY LABORATORY WORKING GUIDELINES

All students must obey Analytical Chemistry Laboratory General Rules below:

- Attendance is compulsory.

- All students must wear **lab coats, goggles/glasses and gloves** at all times.

- Do not eat food, drink beverages, or chew gum in the laboratory.

- No smoking is permitted in the laboratory.

- Do not enter laboratory without your laboratory manual and notebook.

- Each student must read and summarize the necessary parts from the laboratory manual at home and be ready for the laboratory.

- You will take a written or oral entrance quiz at the beginning of each analysis. Their credits will be added your grade.

- Students should work in the lab silently. Moving around banks, talking loudly and going out without permission are forbidden.

- Students are responsible for your cabinet and all equipments entrusted. In addition, All students must purchase these equipments. as follows:

  2 porcelain crucibles, 10 mL pipette, pipette bulb, tongs, spatula, glass rod, goggles 50 mL burette, pH paper, gloves, black, white and blue band filter papers (two each), label or pen for glass and laboratory notebook.

- Broken glass should not be used. Place it in the designated glass disposal container.

- Keep your work space clean and tidy. The working space, desk drawers, cabinets, instruments must be kept neat and clean at all times. Liquid or gas valves must be controlled and turned off at the end of laboratory working at all times.

- Retain all laboratory equipments, materials and chemicals used on the reserved area. When lab work is completed, all materials must be returned to their proper places and used benches, instruments and glassware must be cleaned up.

- Keep analytical balances clean and avoid them dislocate.

GENERAL RULES FOR LABORATORY SAFETY and FIRST AID

- Students must heed what the assistants are told and follow all written and verbal instructions carefully.

- Students must wear lab coats, goggles/glasses and gloves at all times Dress properly during a laboratory activity. Long hair, dangling jewelry, and loose or baggy clothing are a hazard in the laboratory. Long hair must be tied back, and dangling jewelry and baggy clothing must be secured. Shoes must completely cover the foot. No sandals allowed on lab days.

- Check the label on all chemical bottles twice before removing any of the contents. Take only as much chemical as you need with clean pipette or spoon (do not use stock solutions directly).

- Pipette bulbs must always use in order to transfer solutions with pipette, especially for acids and bases.

- Most of the chemicals in the laboratory are toxic and highly corrosive. Avoid contact between these liquids and the skin.

- Perform all work involving hazardous or volatile materials in a fume hood.

- Concentrated acid and base solutions should not pour a sink.

- The Bunsen burner consists of a barrel of an air-regulator, a gas-regulator, and a base. Insufficient air supply causes a yellow flame of incomplete combustion. The experimental apparatus gets covered with soot if it is heated with a yellow flame. In extreme cases, carbon monoxide poisoning might occur. Reduce the air first and reduce the gas next. The reversed operation might cause a backfire in the barrel. If a backfire occurs, immediately turn off the main gas cock without touching the barrel and cool the burner completely with a wet cloth.
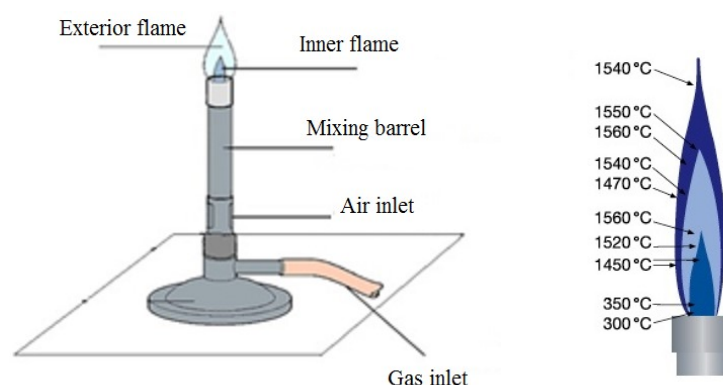
Figure 1. Bunsen burner and its flame.

- Work areas and all glass equipments should be cleaned before you leave laboratory. Wash your hands and check all valves in the laboratory.

- All injuries and accidents must be reported to the instructor.

- While handling flammable liquids such as ether, alcohols, benzene, naked flame (burners, matches) must not be in use. The above liquids must not be stored near radiating heat sources, such as the laboratory oven.

- Volatile liquids and solids that are toxic or irritating should be handled under fume hoods.

- Handling of strong acids and bases requires special attention. When diluting concentrated acids, the acid should be poured into the water and never the opposite.

- The mouth of the glassware containing the solution to be heated should never be pointed toward anyone.

- Become familiar with the location and the use of standard safety features in the laboratory. The laboratory is equipped with fire extinguishers, eye washes, safety showers, fume hoods and first-aid kits.

- Chemical splatters into the eye. First the eyelid should be opened by using the thumb and the pointing finger. Then, by using the eye wash kit, the eye should be rinsed with large amounts of water. When an acid or alkaline solution gets into eye, the eye should be rinsed with 1 % $NaHCO_3$ or 1 % boric acid, respectively. See doctor if necessary.

- Burning: The burned spot on the skin should not be treated with water; rather, a special bandage should be used. See doctor if necessary.

- Poisoning. Prompt medical treatement should be obtained.

FIRST AID AND SAFETY PRECAUTIONS AGAINST ACCIDENTS IN THE LABORATORY

The possibility of accidents happening while working in a chemical laboratory presents certain risks. In order to prevent these accidents and reduce their impact to the minimum, some rules must be followed:

- All accidents must be reported immediately to the responsible Research Assistant, even if considered insignificant.

- Volatile and flammable liquids such as ether and alcohol must not be used near open flames.

- When the liquid in a beaker catches fire, the heat source must be removed immediately and the flame must be extinguished by covering the beaker with a watch glass or wet cloth.

- If rubber hoses of the Bunsen burner have tears or elasticity at the entrance to the burner or gas valve, the rubber hose may catch fire inside. In this case, the gas valve must be closed immediately. It is important to check the hoses used for the burner beforehand, and replace the hoses which are risky for operation safety with new ones.

- You must not lean towards burner when lighting it. This may pose the risk of getting burned.

- When diluting concentrated acids, the acid must always be slowly added to the water. If water is added to the concentrated acids, there may be risk of the acid splashing and burning.

- When a substance is being heated in a tube, it is important for the safety of you and your friends that you do not turn the tube on yourself and your friends.

- When an item is being heated in a tube, the tube must not be held in a constant state and the heating must be done near the upper level of the liquid in the tube with continuous shaking.

Incorrect Correct
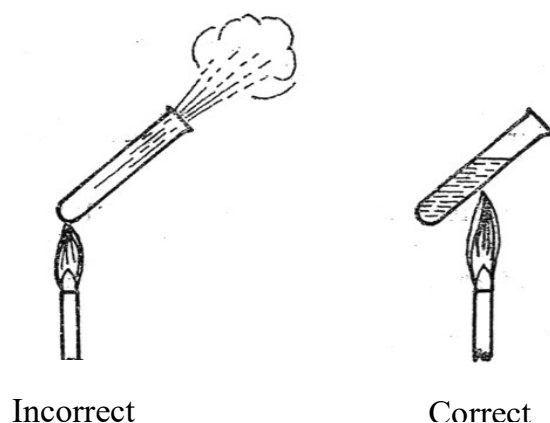
Figure 2. Heating process in tubes.

- If any corrosive chemical splashes on your skin or your eyes, you must rinse immediately with plenty of water and inform the responsible Research Assistant.

- When you need to smell a substance, it is important that you do not smell directly but smell it by pushing the vapors slowly towards your nose with your hands.

- If an acid or base is swallowed, MgO suspension and 15 - 30 mL vinegar must be ingested against acids and bases, respectively.

- Burns from chemical substances should first be washed with plenty of water and then treated with another substance that neutralizes the substance. If an acid is spilled, it must be washed with sodium hydrogen carbonate solution; if a base is spilled, it must be washed with 4% boric acid or 1% acetic acid solution; if bromine (Br_2) solution is spilled, it must be washed with sodium thiosulfate solution. Burn ointment should be applied later.

- During your experiments, your clothes, hands and eyes are protected by wearing laboratory coats, gloves and goggles, respectively.

LABORATORY EQUIPMENTS

Flask
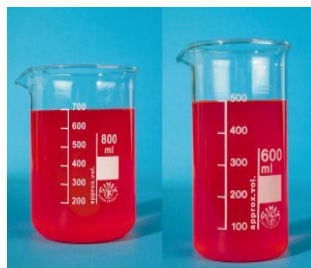
Beaker

Porcelain capsule

Porcelain Crucible

Clay Triangle

Watch Glass

Plastic Bulb

Wooden Forceps

Protective Gloves

Asbestos Mesh

Sheet Foot (tripod)

Burner (Bunsen)

Brush
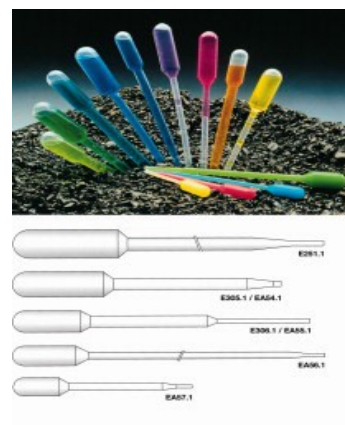
Plastic Pasteur Pipette
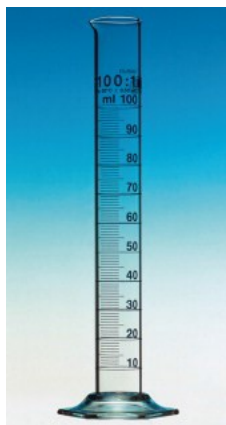
Measuring Cylinder

Wash Bottle

Forceps

Tube holder and test tubes	Centrifuge Tube	Spatula
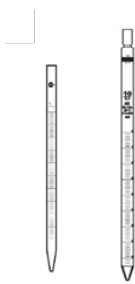
Volumetric flask	Pipette	Volumetric pipette	Burette
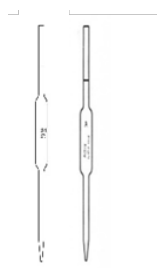
Desiccator	Crucible tongs	Burette clamp	Support

Funnel

Figure 3. Tools and equipment used in qualitative analysis laboratory.
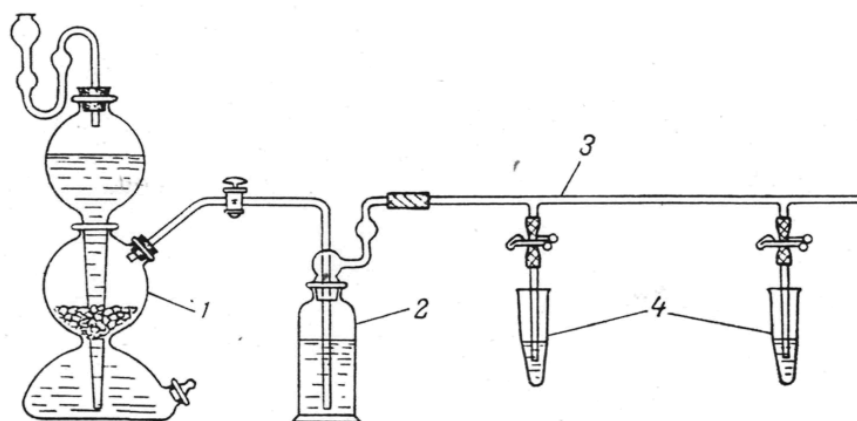
Figure 4. Kipp apparatus used for obtaining hydrogen sulfide gas (1-Kipp apparatus, 2-Washing flask, 3- Hydrogen sulfur gas outlet tube, 4- Tube containing saturated hydrogen sulfide solution).

I- QUALITATIVE ANALYSIS

1. LABORATORY TECHNIQUES

1.1. Separation of precipitates from solutions

In qualitative analysis, the following frequently used methods are applied for the physical separation processes of solid and liquid materials:

1.1.1. Precipitation

Precipitation in qualitative analysis is carried out in a centrifuge tube. The reagent solution is added to a few mL of analysis solution in the tube and mixed slightly. Immediately after addition of the reagent solution, the contents of the tube must be mixed. Mixing after addition of each reagent drop; this provides advantages such as slower formation of precipitate crystals, better separation of solution by centrifugation and adsorption of lower amounts foreign substances. If the resulting precipitate forms a colloidal solution, the tube content is heated for a few minutes in a water bath after addition of the reagent, this will cause a better coagulation and separation.

Once precipitation process is done, it is necessary to check that the precipitation is complete. For this purpose, the precipitate obtained in the reaction is separated by centrifugation and the clear solution in the upper part of the solution is examined for turbidity by adding 1 drop of reagent solution to the upper liquid phase. In case the upper part of the solution remains clear, it is understood that the entire ion previously separated by precipitation has been removed from the solution or the precipitation has been completed. If turbidity occurs in the upper phase after addition of the reagent, more of the reagent solution is added to and mixed with the solution, heated, and centrifuged again. The completeness of precipitation is then rechecked.

1.1.2. Filtration

It is the most widely used separation method in separating solid and liquid phases. Various funnels and filter papers are used for the filtration process. As the pore size of the filter papers used in the laboratory are about 0.001 cm in diameter, solid particles with particle sizes larger than this value are separated from the solution by remaining on the filter paper. In the filtration process, the precipitate that remains on the filter paper placed in the funnel is called residue, and the liquid that passes through the filter paper is called filtrate.

1.1.2.1. Preparation of Filter Papers

The filter paper is prepared by cutting and folding to fit the glass funnel used. As shown in Figure 1.1, the filter paper is cut into square leaves and folded vertically twice, and the free ends are cut in quarter circular shape with a scissor. It is opened into a cone shape with one side having one layer and the other side having three layers. The filter paper prepared in this form is placed in the funnel. The paper must be soaked with solvent prior to filtration.

(a)   (b)   (c)   (d)
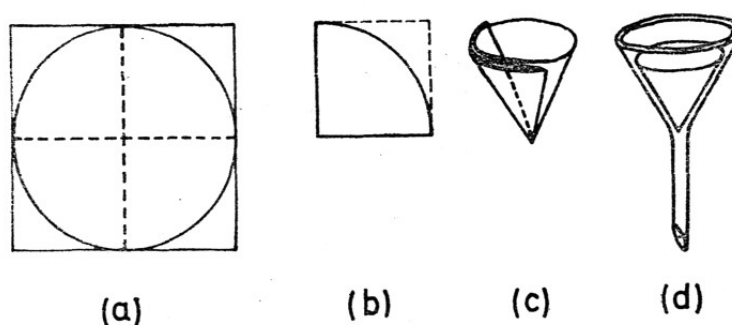
Figure 1.1 Preparation of filter paper.

In cases where the liquid is filtered or the impurities are removed in excess, filtration is accelerated using pleated filter paper. To prepare the pleated filter paper, the filter paper is folded into four segments and after each segment has been folded into two, the eight-sided semicircle is folded once more and placed in the funnel in a cone shape. Figure 1.2 shows the process of preparing pleated filter papers.

(a)   (b)   (c)
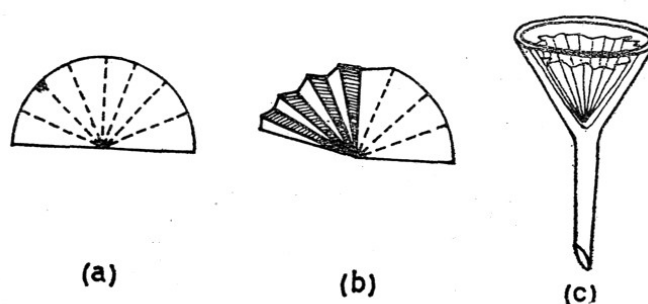
Figure 1.2 Preparation of pleated filter paper.

1.1.2.2. Filtration Process

During filtration, the solutions are always transferred into the funnel along a glass rod as shown in Figure 1.3. The neck portion of the funnel is pressed against the inner surface of the glass container into which the filtrate is collected, so that the capillary action formed by the liquid column transferred into the glass vessel increases the speed of filtration.

Glass rod

Precipitate
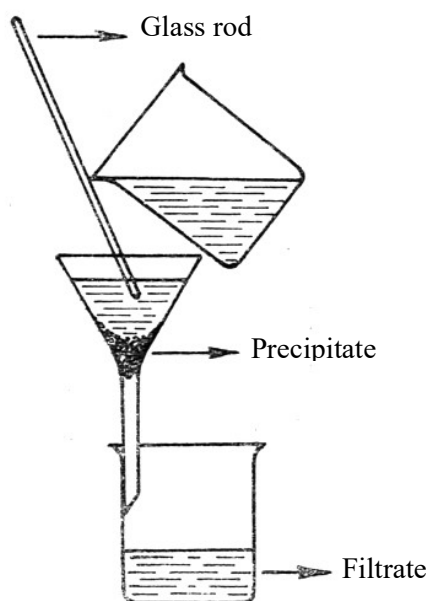
Filtrate

Figure 1.3 Filtration process technique.

1.1.3. Decantation (Transfer)

After precipitation to the bottom of the container (sedimentation), the clear upper part solution can be transferred to another vessel to separate the two phases. This process is called decantation. Figure 1.4 shows the transfer process performed by tilting the beaker in which the precipitate was formed. In the first transfer process, a complete separation cannot be achieved since some solution will be mixed with the precipitate. For this reason, the precipitate is treated and shaken several times with pure solvent and allowed to settle. The upper solution is transferred and a very pure precipitate can be obtained. If the precipitate is formed in the tube, the transfer can be performed by drawing the liquid with a dropper or a Pasteur pipette as shown in Figure 1.5.
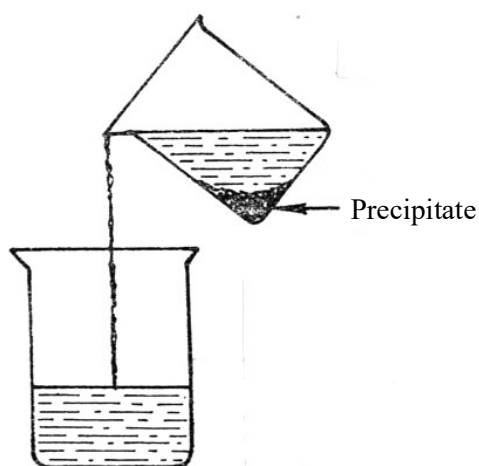
Figure 1.4 Decantation process (I).   Figure 1.5 Decantation process (II).
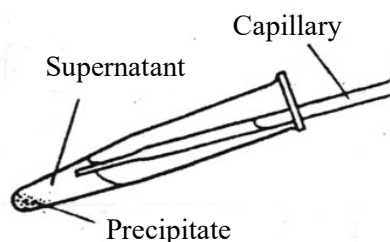
1.1.4. Centrifugation

The precipitation process using the natural gravitational force is improved upon when the centrifugal force of the centrifuge instrument is used. In centrifugation, solid particles in suspension form are separated by the effect of centrifugal force and the separation takes place by easily transferring the transparent upper part solution while the particles adhere to the bottom part of the centrifuge tube. A separation of up to one hundred times that of gravity is achieved with laboratory centrifuges. A very pure precipitate is obtained if the centrifugation is repeated several times with pure solvent after the first separation of the precipitate. Two centrifugal tubes which are identical to each other are used in centrifuge devices. A tube is filled with water to the same level as the mixture to be separated in the other tube. The tubes which are totally identical are placed opposite to each other in the centrifuge device to ensure equilibrium in the device. Figure 4.6 shows a small laboratory centrifuge.

Figure 1.6 An electric centrifuge used in the laboratory.

1.2. Semi-Micro Analysis

Semi-micro qualitative analysis involves the application of reactions which are carried out with reagents and analysis samples that have very small volumes (2-4 mL). The application of these analysis is broad and it includes micro-crystallographic reactions and reactions that are carried out with dropwise volumes of solutions. is widely used. These reactions are sensitive enough to provide qualitative determination of substances in analysis sample at the μg level.

1.2.1. Spot Test

Sensitivity in the reactions carried out on filter paper is considerably higher than in reactions carried out in the test tube due to the adsorption of solvents and substances in the analysis and reagent solutions by paper. Filter papers filled with numerous fine capillaries and large surface area through which the solution can be spread have high adsorptive properties for the materials. For this reason, even a non-selective reaction for the identified ion may become selective if it is carried out on filter paper under appropriate conditions. This feature is frequently used in spot tests for qualitative analysis.

In spot analyzes, reactions take place in the volume of one or more drops of solution on the filter paper. The result of the reaction applied on the paper is a stain showing the presence of the ion having a certain color. Thus, the presence of the ion is detected by qualitative analysis. Characteristics of filter papers used in spot tests include; they must be thicker and more porous compared to others, they must have good adsorption properties, they must not contain mineral salts and they must not leave ashes when they are burned.

1.2.1.1. Application of Spot Test

In spot test analysis, a drop of the reagent solution is dropped onto a capillary strip of filter paper. For this purpose, a pipette capillary tip is immersed 1-2 mm into the reagent solution and the liquid spontaneously rises by capillary action. The tip of the vertically held pipette (Figure 4.7) is placed onto the filter paper and lightly pressed to form a moisture stain of a few mm diameter. Once this is done, the pipette is retracted. After drying the moisture spot in air, one drop of unknown analysis sample solution is applied in the same manner to the center of the spot on the paper. The reaction between analysis sample and reagent through the filter paper capillaries results in colored stains and the paper's color becomes noticeable upon drying in air.

Caution: The solution must not be dropped or shaken onto the paper and the solution must be slowly adsorbed from the capillary end of the pipette. To avoid interference with the reaction, the pipette must be cleaned by contacting it with clean paper and then rinsed with distilled water before it is returned to the bottle. The order of the reagents applied on the filter paper is also important for the test to be successful.
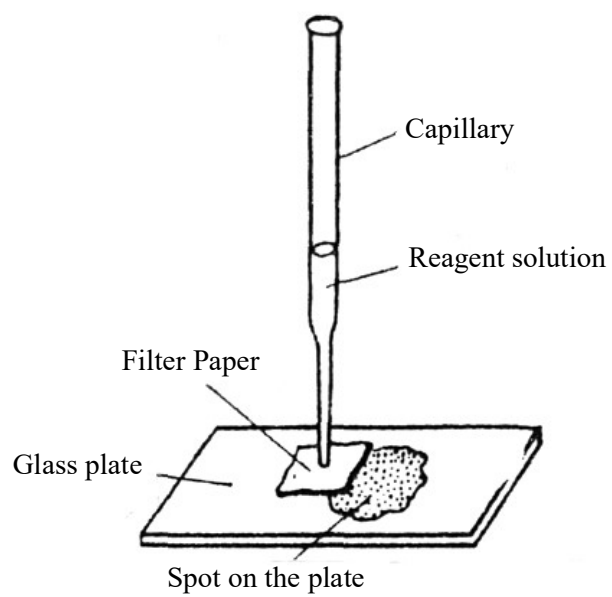
Figure 1.7 Semi micro analysis (spot test) application.

2. THEORETICAL FUNDAMENTALS

2.1. Qualitative Analysis Method

In chemical analysis of an unknown sample, qualitative analysis is first applied, then quantitative analysis is performed. The first objective in chemical analysis is to determine which components form the substance. The basis of qualitative analysis is to bring the substance into a solution form and reacting it with various reagents. The components of the substance are identified based on properties of these reactions. In order for a reaction to be used for analytical purposes, this reaction must have certain properties. These features can be summarized as follows:

a) The reaction should be characteristic. That is; at the end of the reaction, there must be a visible change such as formation of a precipitate, dissolution of the precipitate, discoloration or gas evolution.

b) The reaction must be specific. When a reagent is added to a solution containing many ions, only a single ion must react with this reagent. For example; The dark red color that occurs when a drop of NH4SCN is added to an acidic solution containing Ag^+, Pb^{2+}, Al^{3+}, Ca^{2+} and Fe^{3+} ions is characteristic only for the Fe^{3+} ion. Because, besides Fe^{3+}, the ions in present in this solution do not form a red complex with NH4SCN.

c) The reaction must be sensitive. That is, the reaction must be observable even at low ion concentrations.

The lowest concentration of a substance required to form a reaction that allows its determination is called "**concentration limit**" or "**capture limit**", and is given in g/ml. This value changes from substance to substance, and for the same substance reacting with different reagents.

Qualitative analysis methods are classified according to the amount of substance to be analyzed. The type of method according to the amount of substance analyzed is as follows:

Analysis Method	Weight of Substance Examined
Macro analysis	Greater than 50 mg
Semi-micro analysis	10 - 50 mg
Micro analysis	1 - 10 mg
Ultra-micro analysis	0.001 - 1 mg
Sub-micro analysis	Less than 0.001 mg

In the macro analysis method, both time consuming processes and large quantities of reagents are needed to work with large amounts of samples. Micro-techniques are special techniques, which are carried out with very small tools and require experience. For this reason, semi-micro analysis method is the most appropriate method used in student laboratories where qualitative analysis is being newly learned. Semi-micro analysis method combines the good aspects of other analysis methods and eliminates the negative sides. When compared to macro analysis, this method lowers the usage of reagents, water, energy, amount of toxic gases released from reactions, working space and time. In addition, this method does not require small tools that are difficult to use in other micro methods.

2.2. Chemical Equilibrium and Equilibrium Constant

$$aA + bB \rightleftharpoons cC + dD$$
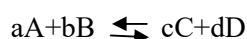
In a general reaction, the state in which the forward reaction rate is equal to the backward reaction is called **chemical equilibrium**. At equilibrium, there is no change in the concentration of reagents and products. This does not mean that the interactions in the reaction are stopped, but the concentrations remain constant due to the forward and backward reaction rates being equal. The equilibrium relation is expressed with the **equilibrium constant** written as K. In the equilibrium expression, products are written as numerator and reactants as denominator. The stoichiometric coefficients (written in lower case) in the reaction are presented as exponents to the chemical species which are written in capital letters. Terms denoted by this expression [ ]; molar concentration of dissolved species and partial pressure (P) in atmosphere for species in the gas phase.

The stoichiometric coefficients used as exponents in square brackets are also used as exponents in the partial pressure expression. Solids and liquids in pure state are not included in equilibrium constant expressions. The equilibrium relationship for the above reaction is given in equation 1. The value of the equilibrium constant K, remains constant as long as the temperature in equilibrium remains unchanged. For this reason, the temperature must be specified when K values are given. If an equilibrium system is being influenced externally (such as temperature, pressure and concentration change or catalyst addition), the system, according to *Le Châtelier's* principle, will move in a direction to eliminate the effect and create a new equilibrium. If the concentration of one of the species in equilibrium is increasing, the system proceeds in a direction to reduce the concentration of the material. A

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change in the amount of any of the species in the reaction, which results in an equilibrium shift is called **mass effect**.

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad (1)$$

2.2.1. Solubility Equilibrium and Solubility Product Expressions

Solubility Equilibrium: It is the moment of dynamic equilibrium in a saturated solution of a solid substance in a liquid solvent, where the rate of dissolution and precipitation of the solid are equal.

The ions of salts such as silver chloride, which have low solubility in aqueous solutions are formed in an equilibrium reaction.

Solubility Product: It is particularly used for salts that are sparingly soluble in water and it is the name given to the equilibrium constant of these salts in saturated solutions.

X_aY_b solubility equilibrium relation of salt = Ksp (Solubility product)

$X_aY_b(k) \rightleftharpoons aX^{+b}(aq.) + bY^{-a} (aq)$
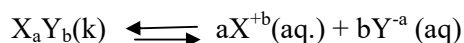
for a reaction,

$Ksp = [X^{+b}]^a [Y^{-a}]^b$

2.2.2. Saturation – Unsaturation and Precipitation

In a dissolution-precipitation reaction, the state of whether a precipitate is formed or not is determined by the precipitated material's ion concentration product (Q).

$Q = Ksp \longrightarrow$ The solution is saturated. Dissolution - precipitation equilibrium has occurred.

$Q < Ksp \longrightarrow$ Solution is unsaturated (no precipitate). A little more dissolution of solid matter is required until the equilibrium is reached.

$Q > Ksp \longrightarrow$ The solution is supersaturated. Some solid materials precipitate in order to attain equilibrium.

2.2.3. Precipitation with H₂S

The large difference in solubility of sulfur compounds with H2S is used to separate group II and III cations. In 0.5 M HCl solution, group II cations are precipitated as sulfides, while group III cations do not form precipitation and remain in solution. The importance of the hydronium ion's concentration stems from its control of the sulfur ion's concentration.

$$H_2S \;+\; 2\,H_2O \;\longrightarrow\; 2\,H_3O^+ \;+\; S^{2-}$$

$$Ka = \; [H_3O^+]^2\,[S^{2-}]\,/\,[H_2S] \; = 6.8 \times 10^{-23}$$

The saturated H₂S solution is approximately 0.1 M. In this case,

$$[H_3O^+]^2\,[S^{2-}] \;=\; 6.8 \times 10^{-24}$$

If the concentration of the hydronium ion which allows the group II cations to precipitate in the form of sulfides is assumed to be 0.3 M (pH = 0.5), S^{2-} ion concentration required to precipitate the cation is:

$$(0.3)^2\,[S^{2-}] = 6.8 \times 10^{-24} \quad [S^{2-}] = 7.5 \times 10^{-23}\ M.$$

In the semi-microanalysis method, the initial concentrations prior to the precipitation of cations are less than or equal to 0.01 M. Taking this fact into considering, the solubility product of a divalent cation (M^{2+}) sulfide is:

$$MS(s) \longrightarrow M^{2+} \;+\; S^{2-}$$

$$Ksp = [M^{2+}]\,[S^{2-}] = (0.01)\,(7.5 \times 10^{-23}) = 7.5 \times 10^{-25}.$$

All the solubility product values of group II cation sulfides obtained in a solution with $[H_3O^+]$ = 0.3 M are less than 7.5 x 10⁻²⁵, but the solubility product values of the group III cation sulfides are greater than 7.5 x 10⁻²⁵. Therefore, only group II cations will precipitate. The pH of the medium needs to be adjusted in order to precipitate group III cations in the form of sulfides.

The required H₂S for the precipitation of group II and III sulfides; various compounds such as thioacetamide ($CH_3C_SNH_2$) and iron sulfide can be obtained. Thioacetamide, which is the most easily obtained compound is proposed for use in place of H₂S. Furthermore, the thioacetamide compound is readily soluble in water and only heating is required to form H₂S, the only disadvantage is it being expensive. Thioacetamide is hydrolyzed into H₂S by heating.

$$CH_3CSNH_2 + 2H_2O \longrightarrow CH_3COO^- + NH_4^+ + H_2S$$

2.2.4. Key Features of Qualitative Analysis Method

Qualitative analysis is performed by:

a) Utilizing properties such as solubility differences, color differences, solubility differences in various solution media of the precipitates formed at the end of the reaction,

b) Utilizing the color differences shown by some ions a burner flame,

c) Utilizing the formation of colored soluble complex ions at the end of reactions,

d) Utilizing the oxidation and reduction properties of ions in a reaction.

3. BASIC PROCEDURES PERFORMED DURING QUALITATIVE ANALYSIS

3.1. Analysis of Solutions

For the systematic analysis of a sample, 1 mL (20 drops) of the prepared sample solution is taken into a centrifuge tube and systematic analysis is started. The remainder of the solution should absolutely be kept. Because at any step of the analysis, it may be necessary to start the analysis from the beginning for various reasons.

Before systematic analysis, the color of the solution can give some preliminary information. However, due to the fact that some colors are close to each other, color dependent test are quite limited. In terms of having an idea, the color of some cation and anion solutions are as follows: Copper ion, blue or blue-green. Aqueous solution containing cobalt(II) ion is pink color, the hydrate ions of copper and cobalt are colored. The nickel ion is green or bluish-green. The manganese(II) ion is pink, but almost colorless in a dilute solution. The color of iron(III) ion varies from yellow to brown depending on the concentration of the solution. Iron(II) ion solution is light green. The chromium(III) ion is dark blue or greenish black. This color difference is caused by the number of water molecules and anions bound to the complex by coordination. Chromate ion is yellow, bichromate ion is orange-red, ferrocyanide ion is light yellow.

3.1.1. Checking the Acidity of Solutions

The precipitation of ions with any reagent or dissolution of the precipitate occurs in an acidic or basic media. For this reason, the acidity or basicity of the solution must be checked and the required solution medium provided before starting operations. In these laboratory studies, a litmus paper or pH paper is used to check whether the solution has acidic or basic properties. The litmus paper is obtained by impregnating an indicator onto a special paper. When the solution dropped on the litmus paper turns red, it means it is acidic but when it turns blue, it means it is basic. The pH paper is used to determine an approximate pH value of the solution. This paper usually produces different shades of color between pH 1-14. Sensitive pH measurement is obtained using tools (devices) called pH-meters. However, the sensitivity of the pH paper is sufficient for the processes in cation-anion analysis. The litmus and pH papers should absolutely not be thrown into solution when checking the acidity of the solution. With the help of a dropper, a drop of the test solution is placed onto a small part of the litmus or pH paper, and the pH value of the solution is determined when the color of the paper is compared

with the color scale of the pH paper. The used litmus or pH papers should not be used for a second time. The value obtained with the pH paper is approximately one value.

3.1.2. Buffer Preparation

Some reactions in systematic analysis occur in a specific pH range. For this reason, the pH of the solution should be kept within a certain range for the duration of the reaction. In the course of analysis, the addition of an acid, base, reagent solution or water to analysis solution causes only minimal changes in the pH value. Buffer solutions are used for this purpose to prevent this change in pH. Buffer solutions are prepared from a weak acid and its salt (acidic buffer), or a weak base and its salt (basic buffer). These solutions counteract the pH change when a certain amount of acid or base is added and the solution is diluted, thus, the pH of the solution changes slightly. For example, when working in a basic buffer environment, it is necessary to add a certain ratio of NH_3 and NH_4Cl to the solution.

3.1.3. Mixing of Solutions

When a solution is diluted or when a reagent is added to the solution, mixing must be performed to homogeneously dilute the solution or to allow the reagent to rapidly react with the solution. The mixing of a solution in a container with a wide opening can be done with magnetic stirrers or it can simply be done with a glass rod. The analysis carried out in this laboratory are done in test or centrifuge tubes. Mixing in these tubes is also done with glass rod. The tube should not be overfilled so that the solution in the tube can be easily mixed and that the solution does not flow out of the tube during mixing. If the amount of solution in the tube is too small, the tube may be held with one hand and the middle finger of the other hand used to hit the bottom of the tube. The tube can also be held between two fingers to mix the solution by shaking from left to right. Problems arise at various stages of the analysis when mixing is not carried out due to incomplete reaction between reagent and solution.

3.1.4. Heating and Evaporation of Solutions

Heating is required for some reactions to occur. Heating can be done on electric heaters such as a heating plate, in water baths or directly on the burner. Heating of solutions in beakers, flasks, porcelain capsule is carried out on electric heaters or on an asbestos mesh on top of a burner. Heating on burner is not applied to easily flammable solutions (such as ether, alcohol,

etc.). In general, a variety of baths such as water bath or electric heaters must be used (Caution: splashing and spillage caused by heating the tubes in open burner causes both material loss and accidents). A water bath is used to heat solutions in tubes. In some operations it may be necessary to reduce the volume of the solution or evaporate it to dryness. If the volume of the solution in the tube is too high and evaporation will take a long time, the solution is transferred slowly into a porcelain capsule and heated slowly. Evaporation till dryness, is done to attain a few drops of solution in the capsule and immediately removed from the heater.

3.1.5. Formation of Precipitates

The reaction of a substance with a reagent to separate the solid product from the solution is called precipitation, and the sedimented solid is called precipitate. An ion in a sample solution is precipitated by conversion to a compound with very low solubility. In the systematic analysis of this laboratory study, precipitation is carried out in a centrifuge tube. The precipitating reagent must be added dropwise to the sample solution until complete precipitation and while precipitation is ongoing, a stirring rod must be used for mixing.

3.1.6. Checking the Completeness of Precipitation

To ensure that the required separation analysis is complete, it should be checked whether the entire ion in the sample solution has formed a precipitate or not. In qualitative studies, this check is made by taking 1-2 drops of clear solution above the precipitate onto a watch glass and adding 1-2 drops of precipitating reagent. If there is a precipitate, precipitation is not complete. In this case, some more precipitating reagent is added to the mixture in the tube and mixed. This process is continued until a precipitate is not seen on the watch glass. However, the precipitating reagent must not be added in excess. This is because the precipitate dissolves in the reactive excess in many cases.

3.1.7. Centrifugation

Centrifugation is carried out to accelerate the separation of the solid phase and the liquid phase of precipitates. (Caution: This process is not performed if there is no solid phase in the solution.)

3.1.8. Separation of precipitates from solution

In order to separate the precipitate from the solution after centrifugation, the tube is held without shaking at a 45 ° angle and a pre-squeezed dropper is immersed into the liquid part of the solution. The dropper is gradually released to allow the solution to fill it. The solution in the dropper is transferred to another tube. This process is continued until no solution remains on the precipitate.
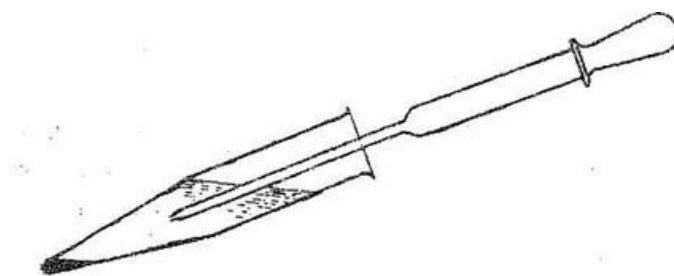

Figure 3.1 Separation of precipitate from solution.

3.1.9. Washing of Precipitates

The precipitate separated from the solution may contain ions of this solution. In order to remove the disruptive effects of these ions, it is necessary to wash the precipitate with a suitable solution. Washing is done with pure water unless otherwise stated. During the washing process, an appropriate amount of washing water is added, mixed with a stirring rod, centrifuged and the solution is discarded. This process is repeated a number of times.

3.1.10. Separation of Precipitates into Sections

In some cases, more than one test may need to be applied to the precipitate. For this, a small amount of pure water is usually added to the precipitate and mixed. A small amount is taken from the mixture with a dropper and transferred into a clean tube. The mixture is centrifuged and the upper solution is discarded. In this way the precipitate can be divided into as many parts as desired.

3.1.11. Dissolution of Precipitates

If the precipitate needs to be dissolved in any solvent, the solution on the precipitate is removed first. Then the solvent is added dropwise to the precipitate while mixing with a stirring rod. This process is continued until the precipitate is fully dissolved, but if needed, a

water bath is used for heating. If the solution on the precipitate is not removed, the solvent effect is reduced due to dilution of the solvent reagent or reaction with the solution.

3.1.12. Flame Test

Elements emit photons at various wavelengths when they are excited by high temperature heating. The eyes can perceive only certain wavelengths. For this reason, colors of some elements in the flame cannot be detected by the naked eye. Group IV and V elements which give characteristic colors in burner flame with a platinum wire are Ba^+ (yellow-green), Na^+ (bright yellow), Ca^{2+} (brick red), K^+ (light purple), Sr^{2+} (carmen red).

Cation sample solutions have to be separated by systematic analysis in order to trace the characteristic color of these cations in the flames. Otherwise, these colors cannot be monitored due to interferences. In systematic analysis, group IV cations are separated into $BaCrO_4$, CaC_2O_4 and $SrSO_4$. These salts are not volatile enough for flame test. For this reason, these salts are converted into their volatile chlorides by dissolving in HCl. The formation of a flame color can be shown for the Ba^{2+} ion by the following reaction equation:

$Ba^{2+}+ 2 Cl^-_{(aq)} \rightarrow BaCl_2$ (solid on platinum wire) $BaCl_2(s) \rightarrow BaCl_2$ (g) $BaCl_2$ (g) $\rightarrow$ Ba (atom) + 2Cl (atom) Ba (atom) $\rightarrow$ Ba* (excited atom) Ba*(excited atom)$\rightarrow$ Ba(atom) + hv (yellow-green color)

The flame test is performed at the top of the inner blue cone of the flame where the temperature is at the highest point. For this test, a 2-3 cm long platinum wire which is attached to a glass rod is used. Before use, the platinum wire should be cleaned by immersing in concentrated HCl solution and heated in the hottest zone of the flame. This process is repeated until the platinum wire does not give color in the flame. The cleaned platinum wire is immersed in the cation solution and the color of the flame is observed. If group V cations such as Na^+ and K^+ ions are present together, the bright yellow color of sodium covers up the light purple color of potassium. In this case a cobalt glass is used. The cobalt glass absorbs the yellow light that sodium emits, allowing the purple light of potassium to be observed. For this reason, the flame test for the potassium ion should be done by looking through a cobalt glass.

3.2. Anion Analysis

3.2.1. Grouping of Anions

It is not possible to divide anions into definite groups, as in cations. However, they can be roughly grouped taking into account their common behavior with some reagents.

Anion Groups:

     Group I: Gives gaseous products as a result of the reaction with dilute HCl and H_2SO_4 acids.

     Group II: Gives low soluble salts in water with some reagents

          a. In a neutral medium with $BaCl_2$ and $CaCl_2$

          b. In 2N HNO_3 medium with $AgNO_3$

     Group III: Reacts as an oxidant with KI and produces I_2

     Group IV: Anions that show reduction properties. These react with MnO_4^-, concentrated HNO_3, H_2SO_4, I_3^- and are oxidized.

     Group V: Non-common reactants.

Preliminary Tests:

Before starting an anion analysis in a sample, preliminary tests are performed to obtain information for subsequent operations. For this purpose, the reaction is monitored by heating the sample with dilute HCl and concentrated H_2SO_4. In Tables 3.1 and 3.2, the behavior of anions against acids are given.

Table 3.1 Effect of dilute HCl

Compound	Gas	Physical Properties of the Gas	Determination of the Gas
Cyanate Carbonate Hydrogen carbonate	CO_2	Colorless, odorless	Blurs the $Ba(OH)_2$ solution which goes with acetic acid. Turns the color of wet blue litmus paper into red color. Puts out the flame.
Sulfide Hydrogen sulfide Thiosulfate Thiocyanate	SO_2	Colorless, tangy	Blurs the $Ba(OH)_2$ solution. Turns the color of dichromate into green, and blue litmus paper into red.
Sulfur	H_2S	Colorless, smelly	Darkens the color of paper soaked in lead acetate.
Nitrite	NO_2	Brown, tangy	Turns the color of iodide with starch into blue-black.
Hypochlorite	Cl_2	Yellow-green, smelly	
Hypobromite	Br_2	Brown, smelly	
Cyanide	HCN	Colorless, almond	Is absorbed on paper soaked in NaOH. Turns dark blue after $FeSO_4$, $FeCl_3$, HCl solutions are added.
Acetate	CH_3COOH	Colorless, vinegar	

Table 3.2 Effect of concentrated H_2SO_4

Compound	Gas	Physical Properties of the Gas	Determination of the Gas
Carbonate Hydrogen carbonate Cyanate	CO_2	Colorless, odorless	Table 7.1
Sulfide Hydrogen sulfide Thiosulfate Sulfate C	SO_2	Colorless, tangy	Table 7.1 Produces sulfur.
Thiocyanate	SO_2	Colorless, tangy	COS burns with a blue flame.
	COS	Colorless, odorless	Properties between CS_2-CO_2.
Chloride	HCl, Cl_2	Light green, smelly	Produces mist in the air. Bleaches litmus paper.
Bromide Hypobromite Bromide	Br_2	Brown, tangy	Turns the color of iodide with starch into blue-black.
Iodide Iodate	I_2	Violet, smelly	Turns the color of starch into blue-black.
Cyanide (free and complex)	CO	Colorless, odorless	Has flammable and reducing properties.
Chloride	Cl_2		
	ClO_2	Yellow, explosive	Has oxidizing properties.
Nitrite Nitrate	NO_2	Red-brown	Oxidizes acidic iodide to iodine. Turns the color of iodide with starch into blue-black.
Acetate	CH_3COOH vapor SO_2 (might occur)	Vinegar	Reacts with Na_2CO_3.
Oxalate Formate Tartarate Citrate	CO CO_2 SO_2		Tartrates rapidly, citrate slowly carbonizes. If water bath is used, citrate turns yellow and tartrate carbonizes.

Another portion taken from the sample is reacted with KI to determine if I_2 is separated. I_2 separation refers to the presence of an anion in the oxidizing property.

Another portion of the solution is treated with MnO_4^- or I_3^- solution. The disappearance of the MnO_4^- or I_3^- solution color shows the presence of a reducing anion in the sample.

Among the redox pairs, the one with the bigger standard reduction potential is reduced, while the smallest is oxidized. In table 3.3 some redox pairs are ordered according to their standard reduction potentials*. Reduced states of the redox pair with smaller standard potential than the MnO_4^- in this chart decolorize MnO_4^-. Likewise, the reduced states of the redox pair with standard potent lower than $I_2/2I^-$ decolorize iodine while the higher ones oxidize iodide to iodide.

Table 3.3. Standard Reduction Potentials for Some Redox Couples

Oxidizing State	Reducing State	E^o (volt)
$S_2O_8^{2-} + 2e^-$	$2\ SO_4^{2-}$	+ 2.01
$H_2O_2 + 2H^+ + 2e^-$	$2\ H_2O$	+ 1.77
$MnO_4^- + 8H^+ + 5e^-$	$Mn^{2+} + 4\ H_2O$	+ 1.51
$ClO_3^- + 6\ H^+ + 6e^-$	$Cl^- + 3\ H_2O$	+ 1.45
$BrO_3^- + 6\ H^+ + 6e^-$	$Br^- + 3\ H_2O$	+ 1.44
$Cl_{2\ (g)} + 2e^-$	$2Cl^-$	+ 1.36
$Cr_2O_7^{2-} + 14\ H^+ + 6e^-$	$2\ Cr^{3-} + 7\ H_2O$	+ 1.36
$ClO_4^- + 8\ H^+ + 8e^-$	$Cl^- + 4\ H_2O$	+ 1.34
$IO_3^- + 6\ H^+ + 6e^-$	$I^- + 3\ H_2O$	+ 1.08
$Br_{2\ (s)} + 2e^-$	$2\ Br^-$	+ 1.07
$NO_2^- + 2\ H^+ + e^-$	$NO_{\ (g)} + H_2O$	+ 1.00
$NO_3^- + 4\ H^+ + 3e^-$	$NO_{\ (g)} + 2\ H_2O$	+ 0.96
$NO_3^- + 2\ H^+ + e^-$	$NO_{2\ (g)} + H_2O$	+ 0.80
$(SCN)_{2\ (g)} + 2e^-$	$2\ SCN^-$	+ 0.77
$BrO_3^- + 3\ H_2O + 6e^-$	$Br^- + 6\ OH^-$	+ 0.61
$AsO_4^{3-} + 2\ H^+ + 2e^-$	$AsO_3^{3-} + H_2O$	+ 0.56
$I_{2\ (k)} + 2e^-$	$2\ I^-$	+ 0.54
$Fe(CN)_6^{3-} + e^-$	$Fe(CN)_6^{4-}$	+ 0.36
$SO_4^{2-} + 4\ H^+ + 2e^-$	$H_2SO_3 + H_2O$	+ 0.17
$S_4O_6^{2-} + 2e^-$	$2\ S_2O_3^{2-}$	+ 0.08
$S_{\ (k)} + 2e^-$	S^{2-}	- 0.48
$2\ CO_2 + 2e^-$	$C_2O_4^{2-}$	- 0.49
$SO_4^{2-} + 2\ H_2O + 2e^-$	$SO_3^{2-} + 2\ OH^-$	- 0.90

*Standard reduction potentials of other redox pair are given in Table Annex-1

3.2.2. Preparation of Sample for Analysis

The acidity of the sample solution is checked with a pH paper. The acidic or basic solution is neutralized before analysis. While the NH_4OH solution is used for neutralization of acidic solutions, diluted HCl or diluted HNO_3 solutions are used for neutralization of basic solutions. The choice of HCl or HNO_3 solutions depends on the analysis scheme to be applied. HCl solution should be used if the analysis is carried out according to Scheme 1 and HNO_3 solution should be used if the analysis is carried out according to Scheme 3. Naturally, the NO_3^- ion is sought in the neutralized solution with HCl, the Cl^- ion in the neutralized solution with HNO_3^-.

During the neutralization of the solution with acids, it must be considered that SO_3^{2-}, HSO_3^-, CO_3^{2-}, HCO_3^-, $S_2O_3^{2-}$, NO_2^-, etc. anions will leave the medium by producing volatile products or decomposing when they are in the acidic medium.

3.2.3. Laboratory Analysis Procedures

For the anion analysis of the sample, the anions are identified using specific recognition reactions after appropriate separation procedures in the following schemes.

Process I.

<u>**Scheme I.**</u>

<u>Stock</u>
~~Solution~~

+ 3.0 M BaCl$_2$

→ **<u>Supernatant I</u>**

<u>Precipitate</u>
(Table 3.4)

Hydrogene carbonate   HCO$_3^-$
Sulfur   S$_2^-$
Bromide   Br$^-$ *
Iodide   I$^-$ *
Thiocyanate   SCN$^-$
Nitrite   NO$_2^-$ *
Nitrate   NO$_3^-$ *
Chlorate   ClO$_3^-$ *
Perchlorate   ClO$_4^-$
Cyanide   CN$^-$
Hydroxide   OH$^-$
Acetate   CH$_3$COO$^-$ *

Table 3.4 The precipitates and colors given by the reactions of anions with 3.0 M $BaCl_2$ in

Precipitates I.

Ion	Precipitate I.	Color	Ion	Precipitate I.	Color
Sulfate*	$BaSO_4$	White	Tellurate	$BaTeO_4$	White
Sulfide	$BaSO_3$	White	Tellurite	$BaTeO_3$	White
Thiosulfate	BaS_2O_3	White	Hexaflorosilicate	$BaSiF_6$	White
Carbonate	$BaCO_3$	White	Silicate	$BaSiO_3$	White
Phosphate*	$Ba_3(PO_4)_2$	White	Bromate*	$Ba(BrO_3)_2$	White
Arsenate	$Ba(AsO_4)_2$	White	Iodate*	$Ba(IO_3)_2$	White
Floride	BaF_2	White	Oxalate*	BaC_2O_4	White
Hexaborate	BaF_6	White	Tartrate	$Ba(C_4H_4O_6)$	White
Tetraborate	BaB_4O_7	White	Citrate	$Ba_3(C_6H_5O_7)_2$	White
Hexacyanoferrate (III)*	$Ba_3[Fe(CN)_6]_2$	White	Hexacyanoferrate (II)*	$Ba_2[Fe(CN)_6]$	Yellow
Molybdate	$BaMoO_4$	White	Chromate*	$BaCrO_4$	Yellow
Selenate	$BaSeO_4$	White	Vanadate	$Ba(VO_4)_2$	Yellow
Selenite	$BaSeO_3$	White	Permanganate	$Ba(MnO_4)_2$	Brown-violet

* Anions to be studied in laboratory samples

Process II:

Scheme II.

Precipitate I.

+ 3.0 M HCl, boiling

Precipitate II.

BaSO$_4$

BaSeO$_4$

BaSiF$_6$

BaWO$_4$

BaSiO$_3$

BaS (S$_2$O$_3^{2-}$)

Supernatant I

PO$_4^{3-}$

AsO$_4^{3-}$

F$^-$

B$_6^{2-}$

MoO$_4^{2-}$

CrO$_4^{2-}$

Fe(CN)$_6^{4-}$

SeO$_3^{2-}$

TeO$_4^{2-}$

TeO$_3^{2-}$

BrO$_3^{2-}$

VO$_4^{3-}$

Anions that leave the medium during Process II:

CO$_3^{2-}$, SO$_3^{2-}$, S$_2$O$_3^{2-}$, Fe(CN)$_6^{3-}$, C$_2$O$_4^{2-}$, C$_4$H$_4$O$_6^{2-}$, C$_6$H$_5$O$_7^{3-}$, IO$_3^-$, MnO$_4^-$

Scheme III.

Stock Solution (Notralized)

Process I.   + 0.1 M AgNO$_3$ → **Supernatant I**

Precipitate I.
AgBr, AgCl, AgI, AgSCN, Ag$_3$[Fe(CN)$_6$], AgIO$_3$, AgBrO$_3$, Ag$_2$SO$_4$, AgCH$_3$COO, AgNO$_2$

Process II.   Aquous suspension, boiling

Supernatant II.
NO$_2^-$
SO$_4^{2-}$
BrO$_3^-$
CH$_3$COO$^-$

Precipitate II.
AgBr, AgCl, AgI, AgSCN, Ag$_3$[Fe(CN)$_6$], AgIO$_3$, AgBrO$_3$

Process III.   + 3.0 M HNO$_3$

Precipitate III.
AgBr, AgI

Supernatant III.

Process III a.   Extraction with ether

Process III b.

Organic acids

Process IV.   + 3.0 M NH$_4$OH

Supernatant IV.
Cl$^-$
CN$^-$
SCN$^-$
Fe(CN)$_6^{3-}$
WO$_4^{2-}$
and some
IO$_3^-$
BrO$_3^-$
Br$^-$

Precipitate IV.
AgBr, AgI

Process V.   concentrated NH$_4$OH

Precipitate V.
AgI

Supernatant V.
[Ag(NH$_3$)$_2$]Br

Process V a.   + HNO$_3$

Supernatant V b.
(not important)

Process VI.   + 3.0 M HNO$_3$
boiling

Supernatant VI.
(not important)

Precipitate VI.
AgI

Supernatant V a.
AgBr

Process VII.   + 3.0 M NH$_4$OH

Precipitate VI.
AgI

Supernatant VII.
Fe(CN)$_6^{3-}$
(Fe(CN)$_6^{4-}$)

Precipitate III b.
(not important)

Supernatant III b.

Process III c.   H$_2$S

Supernatant III c.
PO$_4^{3-}$, CrO$_4^{2-}$, CNO$^-$, VO$_4^{3-}$

Precipitate III c.
Metallic sulfur derived
from oxidation process

41

Table 3.5 Colors and stability properties of silver salts.

Silver Salts	Color	Stability
Sulphite*	White	Darkens when heated.
Thiosulfate*	White	Darkens when heated.
Formate*	White	Darkens easily.
Borate*	White	Darkens easily.
Citrate	White	Decomposes at 100°C.
Carbonate*	Light yellow	Darkens when heated.
Permanganate*	Violet	Decomposes at 100°C.
Chloride	White	
Cyanate*	White	
Cyanide*	White	
Bromate	White	
Iodate	White	
Thiocyanate	White	
Ferrocyanide	White	Oxidized by HNO_3.
Nitrite*	White	
Phosphate	White	
Sulfate	White	
Selenite	White	
Selanit	White	
Tellurium	White	
Tellurate	White	
Vanadate	White	
Molibdate	White	
Acetate	White	
Oxalate	White	
Tartrate	White	
Bromide	Dirty yellow	
Tungstate	Light yellow	
Iodide	Light yellow	
Arsenide	Yellow	
Silicate	Yellow	
Ferricyanide	Orange	
Chloroplatinate	Red	
Chromate	Dark red	
Arsenate	Brown	
Sulfur	Black	

* If the sample is treated with acid, these anions do not precipitate as they leave the medium.

3.3. Identification of Anions

<u>**Arsenate,**</u> AsO_4^{3-}

1. Five (5) drops are taken from Supernatant II given in Scheme II. Ten (10) drops of concentrated HNO_3 and 5 drops of saturated ammonium molybdate solution are added. The appearance of a yellow precipitate without heating indicates the presence of a phosphate anion in the sample. If a yellow precipitate forms when the tube is heated, there is AsO_4^{3-} anion in the sample.

$$H_3AsO_4 + 12(NH_4)_2\,MoO_4 + 21HNO_3 \rightleftharpoons (NH_4)_3\,[As(Mo_3O_{10})_4]\downarrow + 21NH_4NO_3 + 12H_2O$$
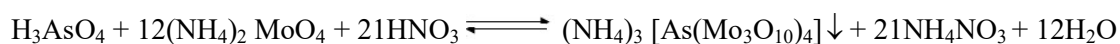
The precipitated ammonium arsenomolybdate (or ammonium molybdate arsenate) is insoluble in concentrated HNO_3, but soluble in ammonium hydroxide and alkali hydroxide.

$$(NH_4)_3\,[As(Mo_3O_{10})_4] + 24NH_4OH \rightleftharpoons (NH_4)_3\,AsO_4 + 12\,(NH_4)_2\,MoO_4 + 12H_2O$$
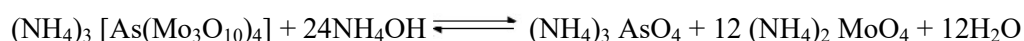
2. In an acidic medium, potassium reacts with iodide solution to form iodine.

$$AsO_4^{3-} + 2I^- + 2H^+ \rightarrow AsO_3^{3-} + I_2 + H_2O$$
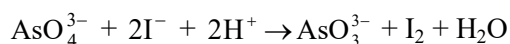
If more iodide is present in the medium, iodine forms the triiodide and remains in the solution.

$$AsO_4^{3-} + 3I^- + 2H^+ \rightarrow AsO_3^{3-} + I_3^- + H_2O$$
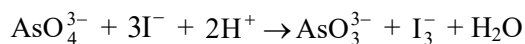
3. If the Precipitate of Scheme IIIc is obtained, it is suspected that AsO_4^{3-} anion is present in the sample.

<u>**Arsenide,**</u> **AsO$_3$$^{3-}$**

The arsenide ion decolorizes the iodine solution by reducing the iodine in weak acidic and basic medium.

$$AsO_3^{3-} + I_3^- + H_2O \rightleftharpoons AsO_4^{3-} + 3I^- + 2H^+$$

The generated H^+ ion must be neutralized so that the reaction can go forward quantitatively. For this purpose adding HCO_3^- to the medium is the most appropriate method.

$$2HCO_3^- + 2H^+ \leftrightarrow 2H_2CO_3 \leftrightarrow 2H_2O + 2CO_2$$

After the oxidation reaction with the iodine solution, the AsO_4^{3-} anion is searched for and an exact decision is made about presence of the AsO_3^{3-} anion in the sample.

Other Reactions:

1. Decolorizes $KMnO_4$ solution.

$$5\,AsO_3^{3-} + 2MnO_4^- + 6H^+ \leftrightarrow 5\,AsO_4^{3-} + 2Mn^{2+} + 3H_2O$$

2. The yellow precipitate with $AgNO_3$ dissolves by NH_3 addition.

$$AsO_3^{3-} + 3Ag^+ \rightarrow Ag_3AsO_3 \downarrow$$

$$Ag_3AsO_3 + 6NH_4OH \leftrightarrow 3[Ag(NH_3)_2]^+ + AsO_3^{3-} + 6H_2O$$

$$2H_3AsO_3 + 6HCI \leftrightarrow 2AsCl_3 + 6H_2O$$

$$2AsCl_3 + 3H_2S \leftrightarrow As_2S_3 \downarrow + 6HCl$$

$$H_3AsO_4 + H_2S \rightarrow H_3AsO_3 + S \downarrow + H_2O$$

$$2H_3AsO_3 + 6HCl \leftrightarrow 2AsCl_3 + 6H_2O$$

$$2AsCl_3 + 3H_2S \rightarrow As_2S_3 + 6HCl$$

$$2H_3AsO_4 + 5H_2S \rightarrow As_2S_5 \downarrow + 8H_2O$$

$$2H_3AsO_4 + 5H_2S \rightarrow As_2S_3 \downarrow + 2S \downarrow + 8H_2O$$

Acetate, CH_3COO^-

1. A few drops of concentrated H_2SO_4 and ethyl alcohol are added to the solid sample. If heated slightly, the characteristic odor of ethyl acetate is felt.

$$CH_3COOH + C_2H_5OH \rightarrow CH_3COO\,C_2H_5 + H_2O$$

2. Acetic acid odor is felt when solid sample is milled together with $KHSO_4$. $AgNO_3$ and $KMnO_4$ should be added to the solid mix in order to remove other volatile and odorous anions. The cyanide, thiocyanate and sulfur anions are separated as $AgCN$, $AgSCN$, Ag_2S. Thiosulfate and sulfite anions are oxidized to sulfate, and nitrite to nitrate with $KMnO_4$.

$$CH_3COOMe + KHSO_4 \rightarrow CH_3COOH + MeKSO_4$$

Borate, BO^{2-} (meta), $B_4O_7^{2-}$ (tetra)

Salts of H_3BO_3, boric acid are unknown. When H_3BO_3 is heated, B_2O_3 is formed over the intermediate product, metaborate acid (HBO_2) and tetraborate acid ($H_2B_4O_7$), which is an acid of medium strength.

$$2H_3BO_3 \leftrightarrow B_2O_3 + 3H_2O$$

1. BO_2^- and $B_4O_7^{2-}$ ions form compounds with heavy metal ions that are poorly soluble in water.

$$2BO_2^- + Ba^{2+} \rightarrow Ba(BO_2)_2$$

$$B_4O_7^{2-} + 2Ba^{2+} + H_2O \leftrightarrow 2Ba(BO_2)_2 + 2H^+$$

Barium metaborate is soluble in HNO_3.

2. The borate ion solution is placed in a test tube and 1 mL of concentrated H_2SO_4 is added. After the solution has cooled, 0.5 - 1 mL of methanol or glycerin is added onto it, then the resulting steam is burned (the tube may be heated if necessary). The boron ester (or boron ethers) formed in the presence of borate gives the flame a luminescent green color.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow 4H_3BO_3 + Na_2SO_4$$

$$H_3BO_3 + 3CH_3OH \rightarrow (CH_3O)_3B + 3H_2O$$

The presence of ions in the sample does not affect the reaction. Because the barium is bound in the form of barium sulfate due to adding H_2SO_4. Make sure that the solution does not spill into the flame. Otherwise, if copper is present in the sample, the flame will have a green color, causing results to be wrong.

*Bromate, BrO^{3-}

1. A few drops from the Supernatant II in Scheme 2 are acidified with dilute H_2SO_4 and 3-5 drops of 0.5 M KBr solution is added.

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

The bromine formed according to the reaction is passed through the organic phase by adding chloroform and shaking. The bromine passing through the chloroform phase gives a yellowish

red color. When the chloroform phase is separated and then rinsed with KI solution, the resulting iodine gives chloroform a violet color.
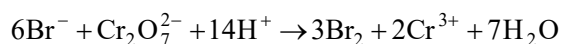
$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

2. The color of the saturated Manganese (II) chloride solution in concentrated HCl is likely to turn brown or gray due to the formation of $MnCl_4^{2-}$ or $MnCl_6^{4-}$ complex ions.

*Bromide, Br⁻

1. A few drops of sample from Supernatant I is acidified with 3.0 M H_2SO_4 then $CHCl_3$ added to form a separate phase. If the medium is shaken after adding chlorine water or permanganate solution, the resulting bromine gives a yellow-red color to the chloroform phase.

$$2Br^- + Cl_2 \rightarrow Br_2 + 2Cl^-$$

$$10Br^- + 2MnO_4^- + 16H^+ \rightarrow 5Br_2 + 2Mn^{2+} + 8H_2O$$

2. 2.5% potassium dichromate solution is added to the sample solution acidified with the sulfate acid dropwise.

$$6Br^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Br_2 + 2Cr^{3+} + 7H_2O$$

When the resulting bromine is passed through the chloroform phase while the green color of the Cr^{3+} ion appears in the aqueous phase, the chloroform phase gets a yellow-red color. Adding excess amounts of dichromate makes it difficult to see the green color.

3. If the Br⁻ containing solution is acidified by the addition of 10% HNO_3 and a 1% $AgNO_3$ solution, a light yellow AgBr precipitate is formed.
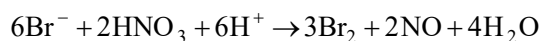
$$Br^- + Ag^+ \rightarrow AgBr$$

AgBr is insoluble in the dilute NH_4OH solution but is soluble in the concentrated NH_4OH solution.

$$AgBr + 2NH_4OH \rightarrow [Ag(NH_3)_2]^+ + Br^- + 2H_2O$$

4. *Other Reactions:*

$$2Br^- + S_2O_8^{2-} \rightarrow Br_2 + 2SO_4^{2-}$$

$$6Br^- + 2HNO_3 + 6H^+ \rightarrow 3Br_2 + 2NO + 4H_2O$$

$$2Br^- + SO_4^{2-} + 4H^+ \rightarrow Br_2 + SO_2 + 2H_2O$$

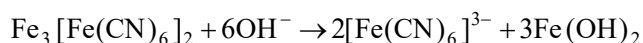## *Ferricyanide, Hexacyanoferrate (III), Fe(CN)$_6^{3-}$

1 drop of 3.0 M H_2SO_4 and 1 drop of 0.3 M of $FeSO_4$ solution is dissolved in 0.3 M H_2SO_4 onto the 1 drop sample taken from the main solution or from the Supernatant IV in Scheme III. The formation of dark blue (Turnbull blue) indicates the presence of ferricyanide ions.
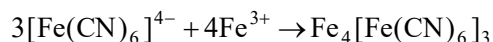
$$3Fe^{2+} + 2[Fe(CN)_6]^{3-} \rightarrow Fe_3[Fe(CN)_6]_2$$

The precipitate is insoluble in dilute HCl, forms alkali metal hydroxides with $Fe(OH)_2$ and decomposes.

$$Fe_3[Fe(CN)_6]_2 + 6OH^- \rightarrow 2[Fe(CN)_6]^{3-} + 3Fe(OH)_2$$

*Ferrocyanide, Hexacyanoferrate (II), Fe(CN)$_6^{4-}$

1 drop of 0.3 M freshly prepared iron (III) chloride solution is added to 1 drop of the Supernatant II in Scheme II. The formation of a dark blue precipitate (Berlin blue) indicates the presence of hexacyanoferrate (II).

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \rightarrow Fe_4[Fe(CN)_6]_3$$

The solution is insoluble in dilute HCl, forms alkali hydroxide and decomposes.

$$Fe_4[Fe(CN)_6]_3 + 12OH^- \rightarrow 4Fe(OH)_3 + 3[Fe(CN)_6]^{4-}$$
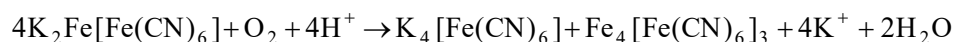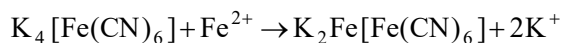
Concentrated mineral acids should not be added on the hexacyanoferrate (II). Decomposes by giving complex anion with condensed acids, HCN and Fe^{2+}.

$$[Fe(CN)_6]^{4-} + 6H^+ \rightarrow Fe^{2+} + 6HCN$$

The precipitate is colored by the presence of oxidizing substances in the medium or by air oxygen (slower) resulting in Berlin blue color.

$$2Fe^{2+} + 1/2O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O$$

$$4Fe^{3+} + 3[Fe(CN)_6]^{4-} \rightarrow Fe_4[Fe(CN)_6]_3 \downarrow$$
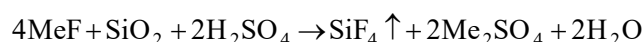
The hexacyanoferrate (II) ion and Fe^{2+} give a white precipitate in the absence of air and a yellowish precipitate with air. By the effect of air, the precipitate gradually becomes colored and dark blue.
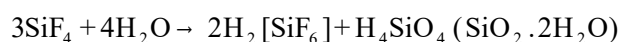
$$K_4[Fe(CN)_6] + Fe^{2+} \rightarrow K_2Fe[Fe(CN)_6] + 2K^+$$

$$4K_2Fe[Fe(CN)_6] + O_2 + 4H^+ \rightarrow K_4[Fe(CN)_6] + Fe_4[Fe(CN)_6]_3 + 4K^+ + 2H_2O$$

Fluoride, F⁻

Unlike other halides (F⁻, Cl⁻, I⁻), the fluoride ion does not form a precipitate with silver nitrate.

1. Fluoric acid readily reacts with SiO_2 and silicates to form silicon tetrafluoride SiF_4. Fluoride is determined using this reaction. If the solid sample is thoroughly mixed with a small amount of finely ground SiO_2 and heated after addition of concentrated H_2SO_4, SiF_4 is formed as a white fog.

$$4MeF + SiO_2 + 2H_2SO_4 \rightarrow SiF_4 \uparrow + 2Me_2SO_4 + 2H_2O$$

If a glass rod with a water droplet on the tip is held in the SiF_4 fog, the water droplet becomes blurry with the formation of silicate acid.

$$3SiF_4 + 4H_2O \rightarrow 2H_2[SiF_6] + H_4SiO_4 \,(SiO_2 . 2H_2O)$$
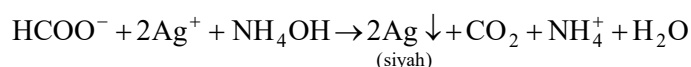
2. Fluoric acid also reacts with metal silicate based glass. Some solid sample are taken into a test tube and 3-4 mL of 25% H2sO4 and a few mL of liquid paraffin are added. When the tube is left in its own state overnight and is washed afterwards, the existence of a matt ring formation around the tube in the area where the paraffin and water phase are combine proves the presence of fluoride.
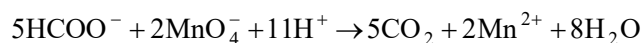
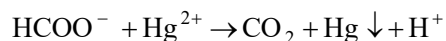$$28HF + \underset{(cam)}{Na_2O.CaO.6SiO_2} \rightarrow 4SiF_4 + Ca[SiF_6] + Na_2[SiF_6] + 14H_2O$$

$$Na_2[SiF_6] + Ca[SiF_6] + 2H_2SO_4 \rightarrow Na_2SO_4 + CaSO_4 + 4HF + 2SiF_4$$

Formate, HCOO⁻

1. It reacts with $AgNO_3$ in ammonia solution to give elemental silver.

$$HCOO^- + 2Ag^+ + NH_4OH \rightarrow \underset{(siyah)}{2Ag} \downarrow + CO_2 + NH_4^+ + H_2O$$

2. It removes the permanganate color in the acidic medium.

$$5HCOO^- + 2MnO_4^- + 11H^+ \rightarrow 5CO_2 + 2Mn^{2+} + 8H_2O$$

3. It reacts with mercury (II) nitrate to form metallic mercury.

$$HCOO^- + Hg^{2+} \rightarrow CO_2 + Hg \downarrow + H^+$$

4. It reduces chromium in the dichromate solution in an acidic medium to give the solution a green color.

$$3HCOO^- + Cr_2O_7^{2-} + 11H^+ \rightarrow 3CO_2 + 2Cr^{3+} + 7H_2O$$

5. If heated with concentrated H_2SO_4, it degrades by giving CO.

$$2HCOO^- + H_2SO_4 \rightarrow 2CO + 2H_2O + SO_4^{2-}$$

*Phosphate, PO4³⁻

10 drops of concentrated HNO_3 and 5 drops of saturated ammonium molybdate solution are added to 5 drops of the sample taken from the Supernatant II in Scheme II. The formation of a yellow precipitate indicates the presence of PO_4^{3-} anion in the sample.
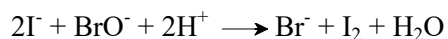
$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \rightarrow (NH_4)_3[P(Mo_3O_{10})_4] + 21NH_4NO_3 + 12H_2O$$

The resulting ammonium molybdatephosphate dissolves in NH_4OH.

$$(NH_4)_3[P(Mo_3O_{10})_4] + 24NH_4OH \rightarrow 12(NH_4)_2MoO_4 + (NH_4)_3PO_4 + 12H_2O$$

Hypobromite, BrO⁻

Hypobromite, which is stable in basic solution, reacts with KI in acidic medium to form iodine.

$$2I^- + BrO^- + 2H^+ \longrightarrow Br^- + I_2 + H_2O$$

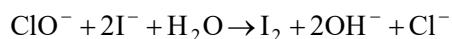## Hypochlorite, ClO⁻

When present in the sample, it disrupts the search for Cl⁻.

1. Forms AgCl precipitation with Ag^+ cation.

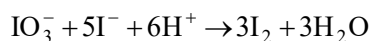$$3ClO^- + 2Ag^+ \rightarrow 2AgCl + ClO_3^-$$

2. The reaction requires acidification of the medium to proceed in the right direction.

$$ClO^- + 2I^- + H_2O \rightarrow I_2 + 2OH^- + Cl^-$$
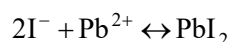
*Iodate, IO$_3^-$

1 - 2 drops of the sample from the Supernatant IV in Scheme III is acidified with concentrated CH_3COOH. 3 drops of $CHCl_3$ and 0.5 M KI solution are dripped onto it. The violet color of the $CHCl_3$ phase indicates the presence of IO_3^-.

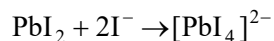$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

*Iodide, I$^-$

1. A few drops of the Supernatant I in Scheme I are acidified with 3.0 M H_2SO_4 and hydrogen peroxide and chloroform are added. If the sample contains iodine, the chloroform phase turns violet. Since the hydrogen peroxide is not influenced by the bromide ion, the reaction is not inhibited.
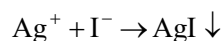
2. The reaction of the iodide solution with the lead acetate solution results with a yellow precipitate. When the precipitate is dissolved in an acetic acid medium by heating and cooled again, crystals appear in the shape of a golden gilt.

$$2I^- + Pb^{2+} \leftrightarrow PbI_2$$

Since the PbI_2 precipitate is slightly dissolved by a complex formation with excess iodide, the excess of lead acetate should be added.
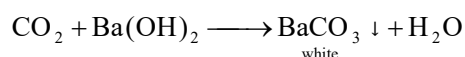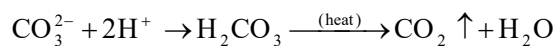
$$PbI_2 + 2I^- \rightarrow [PbI_4]^{2-}$$

3. It yields yellow colored silver iodide precipitate with $AgNO_3$. Unlike AgCl, AgI is insoluble in ammonia solution.

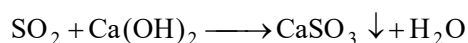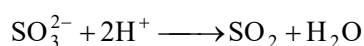$$Ag^+ + I^- \rightarrow AgI \downarrow$$

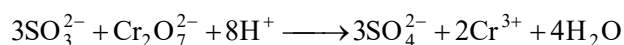**Carbonate and Hydrogen carbonate, CO_3^{2-}, HCO^{3-}**

$*CO_3^{2-}$

1. 3.0 M HCl is added to Precipitate I in Scheme I or the primary sample. If the resulting gas contains CO_2, turbidity will occur when it is passed throuhg lime water or $Ba(OH)_2$ solution.

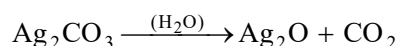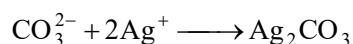$$CO_3^{2-} + 2H^+ \rightarrow H_2CO_3 \xrightarrow{(heat)} CO_2 \uparrow + H_2O$$

$$CO_2 + Ca(OH)_2 \longrightarrow \underset{white}{CaCO_3} \downarrow + H_2O$$

$$CO_2 + Ba(OH)_2 \longrightarrow \underset{white}{BaCO_3} \downarrow + H_2O$$

If sulfide is present in the sample, the analysis is distorted.

$$SO_3^{2-} + 2H^+ \longrightarrow SO_2 + H_2O$$

$$SO_2 + Ca(OH)_2 \longrightarrow CaSO_3 \downarrow + H_2O$$

In this case, the sulfide is firstly oxidized to sulfide with $K_2Cr_2O_7$ or H_2O_2.

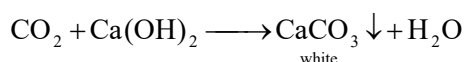$$3SO_3^{2-} + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3SO_4^{2-} + 2Cr^{3+} + 4H_2O$$

2. Carbonate in neutral environment, gives off-white precipitate. When the precipitate is held or heated, the color becomes dark.
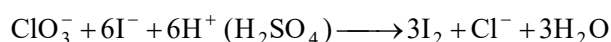
$$CO_3^{2-} + 2Ag^+ \longrightarrow Ag_2CO_3$$

$$Ag_2CO_3 \xrightarrow{(H_2O)} Ag_2O + CO_2$$

HCO_3^-

If a sample taken from Supernatant I in Scheme I is heated, the HCO_3^- anion is degraded by the formation of CO_2.

$$2HCO_3^- \xleftarrow{heat} CO_3^{2-} + CO_2 \uparrow + H_2O$$

$$CO_2 + Ca(OH)_2 \longrightarrow \underset{white}{CaCO_3} \downarrow + H_2O$$
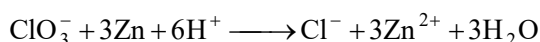
$*Chlorate, ClO_3^-$

1. A few drops of the dilute potassium iodide solution are added to the sample of Supernatant I in Scheme I or several drops taken from the main solution and acidified with a few drops of
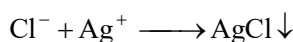
CH$_3$COOH. Then a few drops of CHCl$_3$ are added. Chloroform remains colorless if IO$_3^-$ is not present in the medium because it cannot cause the formation of I$_2$. If IO$_3^-$ is present in the sample, the chloroform phase becomes violet with the formation of I$_2$. In this case, the extraction is continued until all of the IO$_3^-$ in solution is removed and the residual chloroform phase becomes discolored. Then a few drops of concentrated H$_2$SO$_4$ are added. The violet coloration of the chloroform phase indicates the presence ClO$_3^-$ in the sample.

$$IO_3^- + 5I^- + 6H^+ (CH_3COOH) \longrightarrow 3I_2 + 3H_2O$$

$$ClO_3^- + 6I^- + 6H^+ (H_2SO_4) \longrightarrow 3I_2 + Cl^- + 3H_2O$$

2. If Cl$^-$ and ClO$_3^-$ are both in a sample, Cl$^-$ is completely precipitated by the addition of AgNO$_3$ dissolved in 2.0 M HNO$_3$. Chlorate does not precipitate with silver nitrate. After the precipitate is separated by centrifugation, the solution is heated after adding 1 drop of CuSO$_4$ solution and a zinc grain. Chlorate is reduced to chlorine.
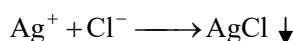
$$ClO_3^- + 3Zn + 6H^+ \longrightarrow Cl^- + 3Zn^{2+} + 3H_2O$$

A white precipitate forms when silver nitrate is added again.

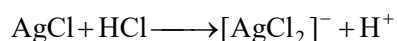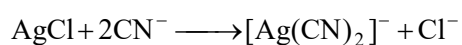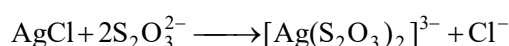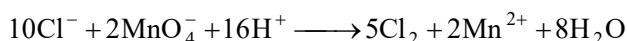$$Cl^- + Ag^+ \longrightarrow AgCl\downarrow$$

*Chloride, Cl$^-$

1. If 2.0 M HNO$_3$ and 1.0 M AgNO$_3$ solutions are dripped into a sample taken from the main solution, a white precipitate is obtained in the presence of chloride. When the medium is made basic by the addition of NH$_4$OH, the precipitate is redissolved by forming a complex and re-precipitates when acidified.

$$Ag^+ + Cl^- \longrightarrow AgCl\downarrow$$

$$AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]^+ + Cl^- + 2H_2O$$

The AgCl precipitate dissolves by forming a complex in S$_2$O$_3^{2-}$, CN$^-$ and concentrated HCl solutions.

$$AgCl + 2S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-} + Cl^-$$
$$AgCl + 2CN^- \longrightarrow [Ag(CN)_2]^- + Cl^-$$
$$AgCl + HCl \longrightarrow [AgCl_2]^- + H^+$$

2. Cl^- ions decolorizes MnO_4^- solution in acidic medium.

$$10Cl^- + 2MnO_4^- + 16H^+ \longrightarrow 5Cl_2 + 2Mn^{2+} + 8H_2O$$

3. Cl^- reacts with brown MnO_2 at high temperatures and Cl_2 gas is formed.
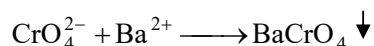
$$2Cl^- + MnO_2 + 4H^+ \longrightarrow Cl_2 + Mn^{2+} + 2H_2O$$

Chromate, Dichromate, CrO_4^{2-}, $Cr_2O_7^{2-}$
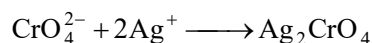
The balance between chromate and dichromate anions is as follows: dichromate in acidic medium and chromate in basic medium.
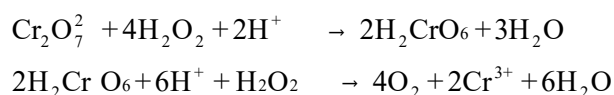
$$Cr_2O_7^{2-} + H_2O \longleftrightarrow 2HCrO_4^- \longleftrightarrow 2H^+ + 2CrO_4^{2-}$$

1. The CrO_4^{2-} anion gives a pale yellow $BaCrO_4$ precipitate with 3.0 M $BaCl_2$ solution. This precipitate is insoluble in CH_3COOH, but soluble in 3.0 M HCl and HNO_3.
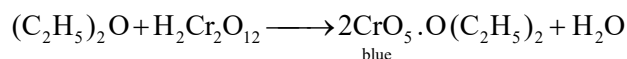
$$CrO_4^{2-} + Ba^{2+} \longrightarrow BaCrO_4 \downarrow$$

2. The CrO_4^{2-} anion gives a deep red precipitate upon addition of $AgNO_3$ solution.

$$CrO_4^{2-} + 2Ag^+ \longrightarrow Ag_2CrO_4$$

3. The dichromate anion reacts with H_2O_2 in acidic medium to give peroxydichromate acid and the solution turns blue. This acid is unstable in the aqueous solution, especially in excess H_2O_2, and the blue color turns green with the formation of Cr^{3+}.

$$Cr_2O_7^2 + 4H_2O_2 + 2H^+ \quad \rightarrow \quad 2H_2CrO_6 + 3H_2O$$
$$2H_2Cr\,O_6 + 6H^+ + H_2O_2 \quad \rightarrow \quad 4O_2 + 2Cr^{3+} + 6H_2O$$

If an ether is present in the medium upon $H_2Cr_2O_{12}$ formation, a new blue colored compound phase is formed on the water upon shaking upon shaking.

$$(C_2H_5)_2O + H_2Cr_2O_{12} \longrightarrow 2CrO_5 . O(C_2H_5)_2 + H_2O$$
$$\text{blue}$$

Procedure: 0.5 mL of ether and 5 mL of 3% H_2O_2 solution are added in a tube and cooled. The sample solution acidified with H_2SO_4 is added after the cooling process. Shake carefully, wait briefly for phase separation.

Other Reactions:

H_2S, SO_2 gases in acidic medium; Cl^-, I^- anions and Fe^{2+} cation turn the color of solution to green by reducing $Cr_2O_7^{2-}$.

$$Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 3S + 7H_2O$$

$$Cr_2O_7^{2-} + 3SO_2 + 2H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$$

$$Cr_2O_7^{2-} + 6Cl^- + 14H^+ \xrightarrow{\text{(ISI)}} 2Cr^{3+} + 3Cl_2 + 7H_2O$$

$$Cr_2O_7^2 + 6I- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Molibdate, MoO_4^{2-}

1. Can be found in Supernatant II under Scheme II (Look for PO_4^{2-})

$$12(NH_4)_2 MoO_4 + H_3PO_4 + 21HNO_3 \longrightarrow (NH_4)[P(Mo_3O_{10})_4] + 21(NH_4)NO_3 + 12H_2O$$
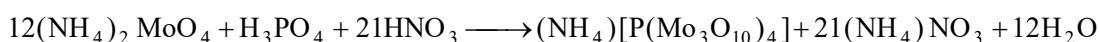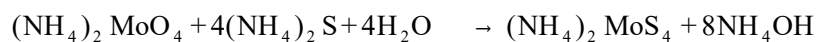
2. A dark red colored thiomolybdate is formed when excess ammonium sulfide is added to the neutral or slightly basic molybdate solution.

$$(NH_4)_2 MoO_4 + 4(NH_4)_2 S + 4H_2O \rightarrow (NH_4)_2 MoS_4 + 8NH_4OH$$

Dark brown MoS_3 precipitates with acidification of the solution.

$$(NH_4)_2 MoS_4 + 2H^+ \longrightarrow MoS_3 \downarrow + 2NH_4^+ + H_2S \uparrow$$

*Nitrate, Nitrite, NO_3^{2-}, NO_2^-

Take 2 - 3 mL of 5% $FeSO_4$ solution dissolved in concentrated H_2SO_4 into a test tube and add 1-2 drops of sample solution. If there is nitrate or nitrite in the sample, the surface of the liquid phase becomes rose color. If the concentration of nitrite or nitrate is high, the surface of the liquid becomes brown. Coloration is caused by the complexation of $FeSO_4$ with NO resulting from the reduction of nitrite or nitrate nitrogen.

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

$$6FeSO_4 + 2HNO_2 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + N_2 + 4H_2O$$

$$2FeSO_4 + 2HNO_2 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NO + 2H_2O$$

$$NO + FeSO_4 \longrightarrow (FeNO)(SO_4)$$

It is fully written as:

$$8FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 2(FeNO)(SO_4) + 3Fe_2(SO_4)_3 + 4H_2O$$

This can be done with the main solution or the sample taken from Supernatant I in Scheme I. However, in the case where I⁻ or Br⁻ is present in the sample, these ions should be separated by precipitation with Ag_2SO_4 first. When the test gives a positive result, it must be determined from which ion it came from. For this purpose, another part taken from the sample is boiled with urea to remove nitrite and then the experiment is repeated. If the result is positive, the presence of nitrate in the sample is proved. However, there is also the possibility of nitrite being present with nitrate. For a definitive conclusion nitrite should be sought by another method.
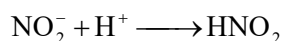
$$2NO_2^- + CO(NH_2)_2 + 2H^+ \longrightarrow 2N_2^\uparrow + CO_2^\uparrow + 3H_2O$$

Acidification of the medium should be done carefully with dilute H_2SO_4. Otherwise, some nitrate acid will form, resulting in a positive result in the next test even though it is not present in the sample.

$$NO_2^- + H^+ \longrightarrow HNO_2$$

$$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$$

Specific Test for Nitrite:

1. If cobalt (II) chloride and potassium chloride solutions are added to the concentrated sample solution and acidified with acetic acid, yellow potassium hexanitrocobaltate (III) precipitates.

$$7NO_2^- + Co^{2+} + 2H^+ + 3K^+ \longrightarrow K_3[Co(NO_2)_6] + NO + H_2O$$

2. If KI solution is added to the sample solution and acidified with acetic acid, nitrite oxidizes iodide to iodine.

$$2I^- + 2NO_2^- + 4H^+ \longrightarrow I_2 + 2NO + 2H_2O$$

Oxalate, $C_2O_4^{2-}$

1. It decolorizes MnO_4^- in the acidic medium.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

2. It takes place in Precipitate I of Scheme I. When $Ba(COO)_2$ is heated, it decomposes by forming CO_2.

$$Ba^{2+} + C_2O_4^{2-} + \longrightarrow \underset{\text{White}}{BaC_2O_4} \downarrow$$

$$BaC_2O_4 + 1/2O_2 \xrightarrow{\text{ısı}} BaCO_3 + CO_2 \uparrow$$

The oxalate ion gives the same reaction as the Ca^{2+} ion.

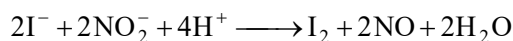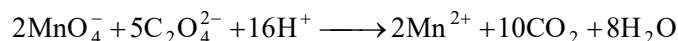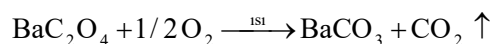**3.** Calcium oxalate is precipitated by adding $CaCl_2$ solution to the sample solution. The precipitate is reacted with dilute H_2SO_4. The soluble fraction is separated, a few drops of sodium vanadate ($NaVO_3$) solution are added and heated. In the presence of oxalate, the colorless solution turns blue.

$$C_2O_4^{2-} + Ca^{2+} \longrightarrow CaC_2O_4 \downarrow$$

$$CaC_2O_4 + H_2SO_4 \longrightarrow CaSO_4 + H_2C_2O_4$$

$$H_2C_2O_4 + 2VO_3^- + 6H^+ \longrightarrow 2VO^{2+} + 2CO_2 + 4H_2O$$

Permanganate, MnO_4^-

Permanganate ion is strongly oxidizing. In an acidic medium, it forms Mn^{2+} ion by reacting with reducing ions like Fe^{2+}, $C_2O_4^{2-}$, S^{2-}, H_2O_2, SO_3^{2-}, I- etc., and the violet color of the solution disappears.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

Permanganate forms MnO_2 precipitate with reducing agents in neutral or basic medium

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_{2\downarrow} + 4OH^-$$

Also;

$$2MnO_4^- + 3Mn^{2+} + 6H_2O \longrightarrow 5MnO_{2\downarrow} + 4H_3O^+$$

Permanganate is oxidized into carboxylic acids in basic medium by organic substances like hydrocarbons, alcohol, aldehyde etc., and it is reduced to MnO_2 or green colored manganese.

$$\underset{\text{toluene}}{C_6H_5CH_3} + 2MnO_4^- \longrightarrow \underset{\text{Benzoate}}{C_6H_5COO^-} + 2MnO_2 + OH^- + H_2O$$

$$2MnO_4^- + \underset{\text{formaldehyde}}{HCHO} + 3OH^- \longrightarrow 2\underset{\text{manganate}}{MnO_4^{2-}} + \underset{\text{formate}}{HCOO^-} + 2H_2O$$

Selenate, Selenite, SeO_4^{2-}, SeO_3^{2-}

Selenium in the high oxidation step is reduced to elemental selenium with many reducing agents.

1. Selenate in a chlorinated acid medium is reduced by iodide into selenium.

$$SeO_4^{2-} + 9I^- + 8H^+ \longrightarrow \underset{\text{Red}}{Se} + 3I_3^- + 4H_2O$$

2. If the selenate solution is heated with concentrated HCl, chlorine gas is released.

$$SeO_4^{2-} + 2HCl \longrightarrow SeO_3^{2-} + Cl_2 + H_2O$$

3. If the selenite solution is reacted with sulfite or SO_2 in concentrated HCl medium, red selenium is formed.

$$SeO_3^{2-} + 2SO_3^{2-} + 2H^+ \longrightarrow Se + 2SO_4^{2-} + H_2O$$
$$H_2SeO_3 + 2SO_2 + H_2O \longrightarrow Se + 2H_2SO_4$$

4. Selenium and Fe (II) sulfate are formed in the chlorine acid medium.

$$SeO_3^2 + 4Fe^{2+} + 6H^+ \rightarrow Se + 4Fe^{3+} + 3H_2O$$

Red Se formed in all reactions is converted into black - gray selenium by boiling in water or by filtering and heating.

Silicate, SiO_3^{2-}

The silicate ion is found only in a basic medium solution, but precipitates as silicate acid in neutral or acidic media.

$$SiO_3^{2-} + 2H_2O \longrightarrow H_2SiO_3 + 2OH^-$$
$$SiO_3^{2-} + 2H^+ \longrightarrow H_2SiO_{3\downarrow}$$

1. If a solution containing ammonium ion is added to a solution ion containing silicate and heated, the silicate acid is precipitated.

$$SiO_3^{2-} + 2NH_4^+ + 2H_2O \longrightarrow H_2SiO_{3\downarrow} + 2NH_4OH$$

2. When sodium fluoride and concentrated H_2SO_4 are added to a solid or dissolved sample and heated, silicon tetrafluoride is formed. When a rod (preferably platinum) with a water droplet at its end is held in the resulting silicon tetrafluoride vapor, the water droplet becomes turbid due to the formation of silicate acid. This process should not be done in the glass container because glass contains silicate. The most suitable vessel is platinum.

$$SiO_3^{2-} + 4F^- + 6H^+ \longrightarrow SiF_4 + 3H_2O$$
$$3SiF_4 + 4H_2O \longrightarrow SiO_2 . 2H_2O_\downarrow + 2H_2SiF_6$$

or

$$SiF_4 + 3H_2O \longrightarrow H_2SiO_{3\downarrow} + 4HF$$

3. The silicate ion reacts with ammonium molybdate in a nitrate acid medium to form a yellow, soluble ammonium molybdatosilicate just as phosphate and arsenate ions.

$$H_2SiO_3 + 12(NH_4)_2MoO_4 + 20HNO_3 \rightarrow (NH_4)_4[Si(Mo_3O_{10})_4] + 20NH_4NO_3 + 11H_2O$$

In the presence of phosphate, the oxalic acid is added to prevent its detrimental effect.

Cyanide, CN⁻

1. 0.5 mL of sample solution is made basic by the addition of 3.0 M NaOH and boiled after adding 1 mL of freshly prepared $FeSO_4$ solution. The solution is then acidified with HCl and the aqueous $FeCl_3$ solution is added. A dark blue precipitate forms in the presence of cyanide. When the cyanide concentration is too low, a blue colloidal solution forms.

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$$
$$Fe(OH)_2 + 6CN^- \longrightarrow [Fe(CN)_6]^{4-} + 2OH^-$$
$$3\ Fe(CN)_6^{\ 4-} + 4Fe^{3+} \longrightarrow Fe_4[Fe(CN)_6]_{3\downarrow}$$
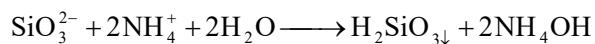
2. One drop each of sample solution and $(NH_4)_2S_2$ solution are added to a watch glass. After evaporation to dryness, 1-2 drops of acidic $FeCl_3$ solution is added dropwise onto the yellow residue. The red color proves the presence of cyanide.

$$CN^- + (NH_4)_2 S_2 \longrightarrow SCN^- + (NH_4)_2 S$$

$$(NH_4)_2 S + 2H^+ \longrightarrow 2NH_4^+ + H_2 S$$

$$n\ SCN^- + Fe^{3+} \longrightarrow [Fe(SCN)_n]^{(3-n)+}$$

n: numbers between 1 and 6.

*Sulfate, SO_4^{2-}

If 3.0 M $BaCl_2$ solution is added to the Supernatant II in Scheme III, the SO_4^{2-} and BrO_3^- anions are precipitated. BrO_3^- ion passes through the supernatant when the resulting precipitate is treated with 3.0 M HCl. $BaSO_4$ remains as a white precipitate.

1. Barium chloride solution is added to the sample solution which is acidified with HCl. Fine particles of $BaSO_4$ precipitate when sulfate is present.

$$SO_4^{2-} + Ba^{2+} \longrightarrow BaSO_4$$

If concentrated H_2SO_4 is added to the precipitate after it is separated, water soluble barium hydrogensulfate is formed.

$$BaSO_4 + H_2SO_4 \longrightarrow Ba(HSO_4)_2$$

2. Sulfate anion reacts with lead acetate solution to form lead sulfate which is insoluble in dilute acids.

$$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$$

$PbSO_4$ is dissolved in concentrated solutions of H_2SO_4, ammonium acetate and ammonium tartrate.

3. If permanganate and barium chloride solutions are added in turns to a solution containing sulfate ion, the permanganate remains in the crystalline network of barium sulfate formed and the precipitate becomes rose-colored. If 3% H_2O_2 is added to the medium, the precipitate retains the color as the solution becomes colorless.

Sulfite, SO_3^{2-}

1. It is found as $BaSO_4$ in Precipitate I. of Scheme I. precipitate (I). If the precipitate is treated with 3.0 M HCl, SO_2 is formed.

$$\text{BaSO}_3 + 2\text{HCl} \longrightarrow \text{BaCl}_2 + \text{SO}_2 + \text{H}_2\text{O}$$

If a litmus paper moistened with water is held over the gas formed, the color becomes red first, then gradually fades.

$$\text{SO}_2 + \text{H}_2\text{O} \longleftrightarrow \text{H}_2\text{SO}_3 \longleftrightarrow \text{H}^+ + \text{HSO}_3^- \longleftrightarrow 2\text{H}^+ + \text{SO}_3^{2-}$$

2. The sulfite ion reacts with the strontium ion similarly to the barium ion.

$$\text{Sr}^{2+} + \text{SO}_3^{2-} \longrightarrow \text{SrSO}_{3\downarrow}$$

White colored strontium sulfide also dissolves in acids by giving SO_2.

3. $SO_3{}^{2-}$ ion gives white precipitate with silver nitrate and is soluble in excess of sulfide. If the silver sulfite precipitate is boiled in solution, it decomposes to form a brownish silver oxide.

$$\text{SO}_3^{2-} + 2\text{Ag}^+ \longrightarrow \text{Ag}_2\text{SO}_3$$

$$\text{Ag}_2\text{SO}_3^- + 3\text{SO}_3^{2-} \longrightarrow 2[\text{Ag(SO}_3)_2]^{3-}$$

$$\text{Ag}_2\text{SO}_3 \xrightarrow{\text{(heat)}} \text{Ag}_2\text{O} + \text{SO}_2$$

4. The precipitate is treated with HCl after the sulfite solution is precipitated directly or in the form of $BaSO_3$ or $SrSO_3$.

$$\text{SO}_3^{2-} + 2\text{H}^+ \longrightarrow \text{SO}_2^\uparrow + \text{H}_2\text{O}$$

$$\text{BaSO}_3 + 2\text{H}^+ \longrightarrow \text{SO}_2^\uparrow + \text{Ba}^{2+} + \text{H}_2\text{O}$$

SO_2 gas is formed when the solution is heated. Filter paper soaked with $FeCl_3$ and $K_3Fe(CN)_6$ solution turns Turnbull bluish color if held over the gas formed.

$$2\text{Fe}^{3+} + \text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{Fe}^{2+} + \text{H}_2\text{SO}_4 + 2\text{H}^+$$

$$3\text{Fe}^{2+} + 2[\text{Fe(CN)}_6]^{3-} \longrightarrow \text{Fe}_3[\text{Fe(CN)}_6]_2$$

Sulfur, S²⁻

The S^{2-} ion forms water-insoluble metal sulfides with many metal ions. Some of them are insoluble in dilute mineral acids. However, by heating with concentrated acids, it is possible to dissolve most of the metal sulfides with H_2S formation.

$$\text{MeS} + 2\text{H}^+ \longrightarrow \text{Me}^{2+} + \text{H}_2\text{S}^\uparrow$$

For this reason, the presence of sulfur in a sample is usually determined on the basis of H_2S formation. H_2S is recognized as follows.

1. Water soluble lead salts form a lead hydroxide precipitate with the sodium hydroxide solution. Lead hydroxide and most lead salts which are insoluble in water like $PbSO_4$, dissolve in sodium or potassium hydroxide solution in the form of plumbite.

$$Pb^{2+} + 2OH^- \longrightarrow Pb(OH)_{2\downarrow}$$
$$Pb(OH)_2 + 2OH^- \longrightarrow [Pb(OH)_4]^{2-}$$
$$PbSO_4 + 4OH^- \longrightarrow [Pb(OH)_4]^{2-} + SO_4^{2-}$$

When a filter paper soaked with plumbite solution makes contact with H_2S, the formation of PbS results ins bright brown-black metallic colored paper.

$$[Pb(OH)_4]^{2-} + H_2S \longrightarrow PbS_\downarrow + 2OH^- + 2H_2O$$

The same test can be done using paper soaked with lead acetate solution.

*Thiocyanate (Rodanide), SCN⁻

The rodanide ion is decomposes with concentrated HCl, concentrated H_2SO_4, dilute and concentrated HNO_3. For this reason, care must be taken when the sample is being acidified.

$$SCN^- + 2H_2SO_4 + H_2O \longrightarrow \underset{carbon\ oxysulfide}{COS} + NH_4HSO_4 + HSO_4^-$$

$$3SCN^- + 8HNO_3 + 2H_2O \longrightarrow 3CO_2 + 3NH_4^+ + 3SO_4^{2-} + 8NO$$

1. The SCN⁻ ion forms a dark red complex depending on its concentration with dilute $FeCl_3$ solution.

$$Fe^{3+} + SCN^- \longrightarrow [Fe(SCN)]^{2+}$$
$$Fe^{3+} + 2SCN^- \longrightarrow [Fe(SCN)_2]^+$$
$$Fe^{3+} + 6SCN^- \longrightarrow [Fe(SCN)_6]^{3-}$$

If fluorine is added to the iron thiocyanate complex, the red color disappears. In addition, oxalic acid and phosphate acid solutions also form a strong complex with Fe, thus clears the color of the iron thiocyanate solution.

2. Concentrated cobalt (II) forms a blue-colored, water-soluble tetrathiocyanate cobalt (II) complex with a nitrate solution.

$$Co^{2+} + 4SCN^- \longrightarrow [Co(SCN)_4]^{2-}$$

This complex is especially unstable in aqueous solution. The blue color disappears when the solution is diluted. The complex is more stable in the organic phase. For this reason it is better to extract it to the ether or isoamyl alcohol phase.

3. Hg^{2+} and Ag^+ ions are precipitated as salts that are poorly soluble in water, then dissolves in excess of thiocyanate with the complex formation.

$$Ag^+ + SCN^- \longrightarrow AgSCN\downarrow$$

$$AgSCN + SCN^- \longrightarrow [Ag(SCN)_2]^-$$

Thiosulfate, $S_2O_3{}^{2-}$

There is no known free thiosulfate acid. Thiosulfate salts are generally stable compounds. However, thiosulfates of some heavy metals are decomposed with water.

1. It is found as BaS_2O_3 in Precipitate I. of Scheme I. BaS_2O_3 is slightly soluble in water but decomposes in dilute mineral acids.

$$BaS_2O_3 + 2H^+ \longrightarrow SO_2 + S + Ba^{2+} + H_2O$$

2. The thiosulfate gives a white silver thiosulfate precipitate with silver nitrate solution. The precipitate dissolves in excess of the thiosulfate. If no thiosulfate is added, the precipitate will decompose with water shortly to form black silver sulfur.

$$S_2O_3^{2-} + 2Ag^+ \longrightarrow Ag_2S_2O_3$$

$$Ag_2S_2O_3 + 3S_2O_3^{2-} \longrightarrow 2[Ag(S_2O_3)_2]^{3-}$$

$$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$$

Cu^{2+} and Pb^{2+} ions also give similar reactions. However, Cu^{2+} is reduced during the reaction.

$$3S_2O_3^{2-} + 2Cu^{2+} \longrightarrow Cu_2S_3O_3 + S_4O_6^{2-}$$

$$Cu_2S_2O_3 + H_2O \longrightarrow Cu_2S + H_2SO_4$$

3. Thiosulfate is oxidized with halogens. Oxidation is carried out to sulfate formation with Cl_2 and Br_2. If I_2 is used it ends in tetrathionate formation.

$$S_2O_3^{2-} + 4Cl_2 + 5H_2O \longrightarrow 2HSO_4^- + 8HCI$$

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

4. Degrades when heated with acids and bases.

$$S_2O_3^{2-} + 2H^+ \longrightarrow SO_2 + S + H_2O$$

$$2Na_2S_2O_3 \xrightarrow{(OH^-)} Na_2S + Na_2S_3O_6$$

5. If the ammonium molybdate solution is added to the thiosulfate solution, mixed carefully, and after adding concentrated H_2SO_4, a molybdenum blue ring forms at the interface between the acid and the aqueous phase. The presence of other reductants disrupts this reaction.

4. CATION GROUPS IN SYSTEMATIC ANALYSIS

Identification of cations by categorization is called systematic analysis of cations. A solution containing a large number of cations can be subjected to qualitative analysis by orderly adding appropriate reagents. The categorization of cations is based on the fact that the solubilities of their chloride, sulfide, hydroxide, carbonate and phosphate salts are different. In such an analysis, the cations are first converted to the chloride, sulfide, hydroxide, carbonate or phosphate salts with appropriate reagents to form four groups of residues; and the last group is separated into a filtrate containing cations that cannot be precipitated with a common reagent. Following the appropriate settling sequence, the cations can be grouped into the following five groups according to the precipitant reactive species:

1. HCl Group: cations separated by precipitation in the form of chlorides in 1 N HCl.

2. H$_2$S Group: cations separated by precipitation in the form of sulfide with H$_2$S in the presence of 0.3 N HCl.

3. (NH$_4$)$_2$S Group: cations precipitated in the form of sulfide or hydroxides with (NH$_4$)$_2$S at pH 8-9.

4. (NH$_4$)$_2$CO$_3$ Group: cations separated by precipitation in the form of carbonates with (NH$_4$)$_2$CO$_3$ at pH 8-9 cations.

5. Groups without a Common Reactive Partner: Cations outside the above groups that cannot be precipitated with a single reagent.

The cations should be separated into groups and separation must be according to the above order. This is because the next reagent also precipitates the cations in the previous group. For example, ammonium sulfide also precipitates cations in the hydrogen sulfide group. Given the sequence of separation, the groups of systematic analysis can also be expressed by numbers. According to this;

HCl group; First Group, H$_2$S Group; Second Group, (NH$_4$)$_2$S Group; Third Group, (NH$_4$)$_2$CO$_3$ Group; Fourth Group, The non-reactive group; can be called the Fifth Group.

In this nomenclature, it should not be forgotten that the majority of the cations in the fifth group are in the first group of the periodic system, all of the cations in the fourth group are in the II group of periodic system. There are also authorities that label analysis groups by looking at the position of elements in the periodic system that become cations:

HCl group is the fifth group, H$_2$S group is the fourth group, (NH$_4$)$_2$S group is the third group,

$(NH_4)_2CO_3$ group is the second group, and the non-reactivity group is the first group.

The right way to group them is **according to the common reagent** rather than numeric expressions, where **the numbers given in the order of separation** must be understood when the groups are stated numerically. For example, HCl group refers to the first group, H_2S group refers to the second group, etc. The group numbers and precipitants formed by the cations relative to the precipitants and their color are given in Table 4.1 below.

Table 4.1 Cation groups and their precipitates

Group	Precipitation Medium	Cation	Precipitate and Its Color
1	Precipitate in chloride form with diluted HCl	Ag^+ Pb^{2+} Hg_2^{2+}	AgCl (white) $PbCl_2$ (white) Hg_2Cl_2 (white)
2	Precipitate in sulfide form with H_2S in diluted HCl medium	Hg^{2+} Cu^{2+} Bi^{3+} Pb^{2+} Cd^{2+} As^{3+}, As^{5+} Sb^{3+}, Sb^{5+} Sn^{3+}, Sn^{4+}	HgS (black) CuS (black) Bi_2S_3 (brown-black) PbS (black) CdS (yellow) As_2S_3 (yellow) As_2S_5 (yellow) Sb_2S_3 (orange-red) Sb_2S_5 (orange) SnS (brown) SnS_2 (yellow)
3	Precipitate in hydroxyl form with diluted NH_3 solution in NH_4Cl medium and sulfide form with H_2S in diluted NH_3 solution	Al^{3+} Cr^{3+} Fe^{3+} Fe^{3+} Mn^{2+} Ni^{2+} Co^{2+} Zn^{2+}	$Al(OH)_3$ (white) $Cr(OH)_2$ (green) $Fe(OH)_3$ (brown) Fe_2S_3 (black) MnS (light pink) NiS (black) CoS (black) ZnS (white)
4	Precipitate in carbonate form with $(NH_4)_2CO_3$ in NH_3 and NH_4Cl medium or precipitate in phosphate form with $(NH_4)_2HPO4$ in strong NH_3 medium	Ba^{2+} Sr^{2+} Ca^{2+} Mg^{2+} Ba^{2+} Sr^{2+} Ca^{2+} Mg^{2+}	$BaCO_3$ (white) $SrCO_3$ (white) $CaCO_3$ (white) $MgCO_3(NH_4)_2\backslash CO_3.4H_2O$ (white) $Ba_3(PO_4)_2$ (white) $Sr_3(PO_4)_2$ (white) $Ca_3(PO_4)_2$ (white) $MgNH_4PO_4.6H_2O$ (white)
5	There is no specific precipitant	NH_4^+ Na^+ K^+	- - -

Separation of cations into groups in a solution is presented in **Scheme 5**, **general separation methods** are presented in **Schemes 6, 7, 8, 9, 10 and 11** for systematically separating cations in each group for informational purposes.

For the studies carried out **in the student laboratory**, the alternative systematic analysis methods mentioned in **Schemes 12, 13, 14 and 15** is expected to be used. There are other systematic separation methods besides the methods given in these diagrams, but the commonly used methods are presented here. The identification experiments used in the diagrams are explained in detail on the page where the relevant cation is found.

SCHEME 5: Categorization of Cations

Stock Solution

+**HCl** (1 M)

HCl filtrate

+ NH$_4$OH, pH~ 0,5 (0,3 M HCl)
+ **H$_2$S**

H$_2$S filtrate

+ pH 8 – 9 (NH$_4$OH-NH$_4$Cl buffer)
+ **(NH$_4$)$_2$ S**

(NH$_4$)$_2$ S filtrate

1. + HCl and heated
2. + pH 9 (NH$_4$OH-NH$_4$Cl buffer),
3. + **(NH$_4$)$_2$ CO$_3$**, heated to 80^{0}C

(NH$_4$)$_2$ CO$_3$ filtrate

Residue Group I	Residue Group II	Residue Group III	Residue Group IV	Residue Group V
AgCl	PbS	FeS	CaCO$_3$	Li$^+$
Hg$_2$Cl$_2$	CuS	MnS	SrCO$_3$	Na$^+$
PbCl$_2$	HgS	NiS	BaCO$_3$	K$^+$
TlCl	Bi$_2$S$_3$	CoS		Mg^{2+}
H$_2$WO$_4$	SnS	ZnS		NH$_4^+$
	SnS$_2$	Cr(OH)$_3$		
	Sb$_2$S$_5$	Al(OH)$_3$		
	As$_2$S$_3$			
	As$_2$S$_5$			
	Au$_2$S$_5$			
	PdS			
	Se			
	Te			
	TeS$_2$			
	MoS$_3$			

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SCHEME 6: Systematic Analysis of Cations in Group I

```
Residue
Group I
   |
   | + H₂O (hot)  ────────────────────────────────→  Filtrate
   |                                                  Pb²⁺, Tl⁺
   ↓                                                     |
Residue I                                                | +3N H₂SO₄, + heat
AgCl, Hg₂Cl₂,                                             |
H₂WO₄                                                     ├──────→  Filtrate
   |                                                      |         Tl⁺
   | +(2-3) M NH₄OH                                        |            |
   |                                                       |            | +%10 KI
   |            Filtrate                                   |            |
   ├─────────→  [Ag(NH₃)₂]⁺                                 |            ├──→ The filtrate is
   |            WO₄²⁻                                       |            |     removed
   |               |                                       |            |
   |               | +%10 KI                               |            |
   |               |                                       |            |
   |               |          Filtrate                     |            |
   |               ├────────→ WO₄²⁻                         |            |
   |               |             |                         |            |
   |               |             | +3,0 M HCl              |            |
   |               |             ├──→ The filtrate is       |            |
   |               |             |     removed             |            |
   ↓               ↓             ↓                         ↓            ↓
Black Residue   Yellow       Dirty White            White        Yellow
                Residue      Residue                Residue      Residue

Hg⁺ NH₂HgCl     AgI          H₂WO₄                  PbSO₄        TlI
```

SCHEME 7: Systematic Analysis of Cations in Group II
(Separation of Copper and Arsenic Sub-groups, and Systematic Analysis of Copper Sub-group)

PtS_2, Au_2S_3, HgS, PbS, Bi_2S_3, CdS, PdS, CuS, As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS, SnS_2, Se, Te, TeS_2, MoS_3

$+(NH_4)_2\,S_x$, and heated to 40^0C in a water bath

I -A (Copper Subgroup)

II − B (Arsenic Subgroup)

PtS_3^{2-}, AuS_2^-, MoS_4^{2-}, SnS_3^{2-}, SbS_4^{3-}, AsS_4^{3-}, (Se, Te dissolve in elemental form)

Residue
PtS_2, Au, HgS, CuS, CdS, Bi_2S_3, PdS, PbS

$+2.0$ M NHO_3, $+$ heat

Residue
PtS_2, Au, HgS

$+(HCl + Br_2)$, $+$ heat
The residue is discarded

Solution
$PtCl_6^{\,2-}$, $AuCl_4^{\,-}$, Hg^{2+}

$+(KCl + HCl$, and concentrated by heating

Residue
K_2PtCl_6

Solution
$AuCl_4^{\,-}$, Hg^{2+}

Excess HCl is evaporated
$+ (NaOH + H_2C_2O_4)$

Residue
Au

Filtrate
$HgCl_2$
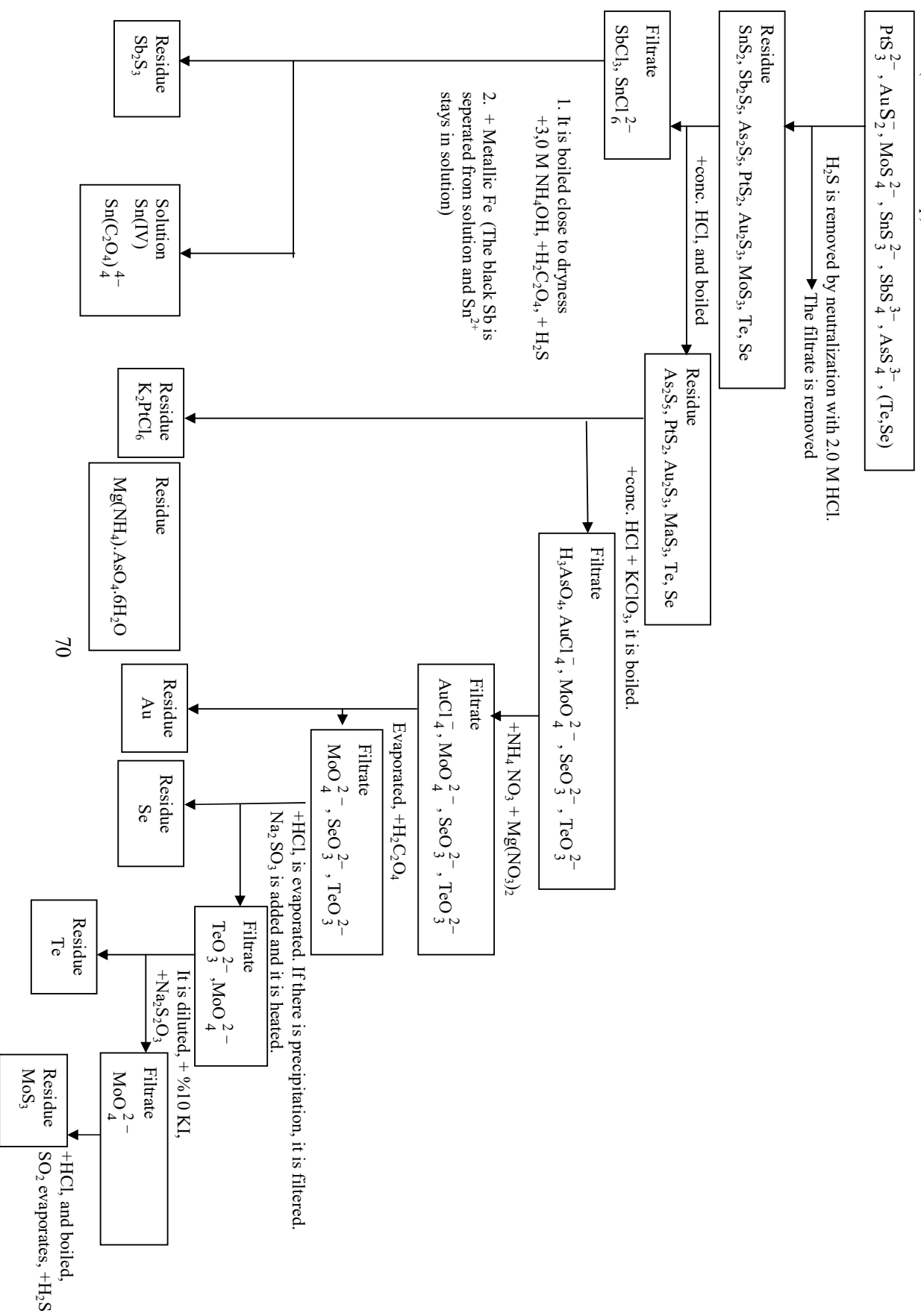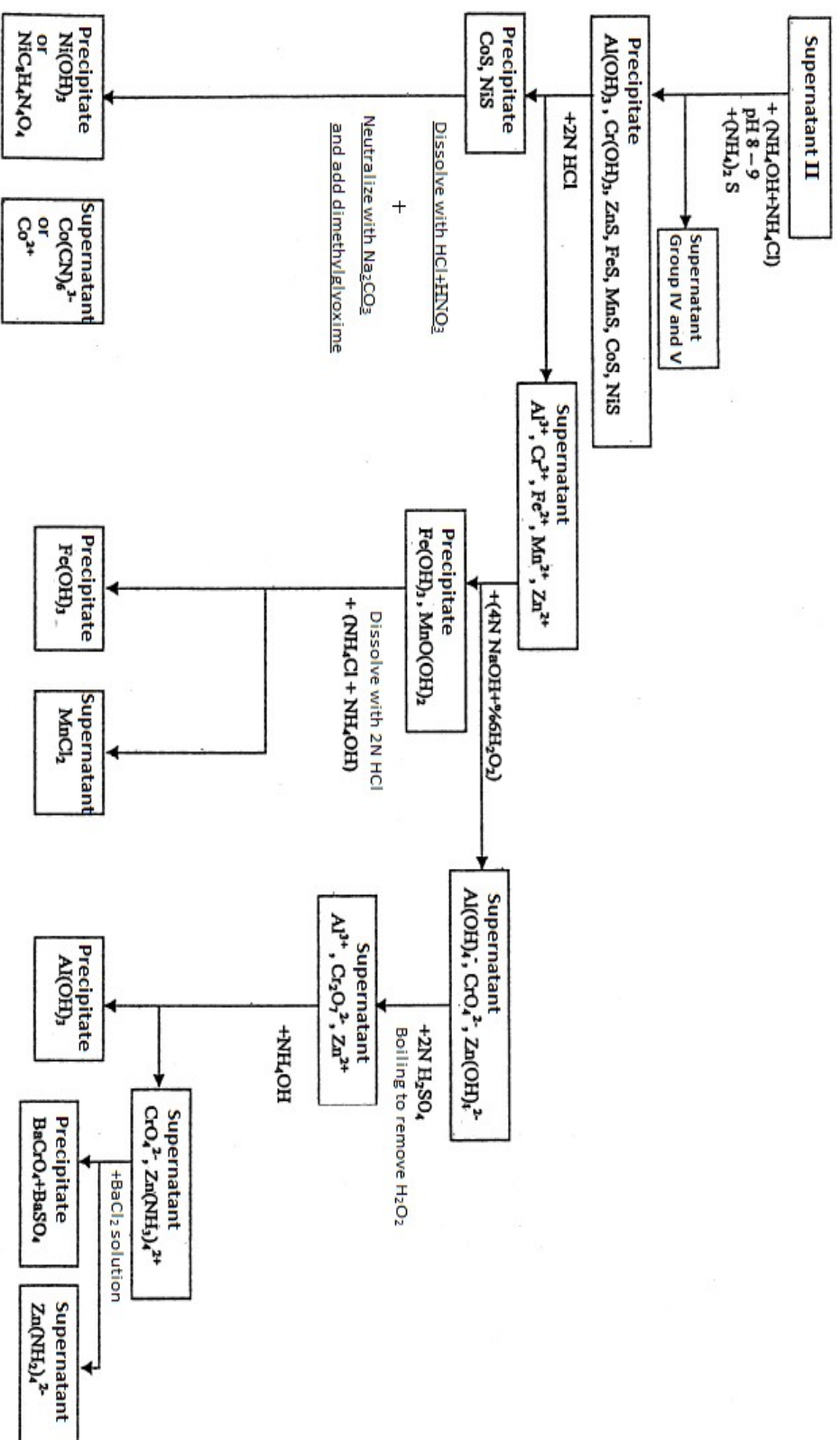
Filtrate
Pb^{2+}, Bi^{3+}, Cd^{2+}, Pd^{2+}

$+H_2SO_4$ (1:1), it is evaporated till white smoke comes out.

Residue
$PbSO_4$ 69

Filtrate
Bi^{+3}, Cd^{2+}, Pd^{2+}, Cu^{2+}

$+$ conc. NH_4OH, and neutralized.

Residue
$Bi(OH)_3$
$BiO(OH)$

Filtrate
$[Cd(NH_3)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$, $[Pb(NH_3)_4]^{2+}$

$+KCN + H_2S$

Residue
CdS

Residue
$[Cu(CN)_4]^{3-}$, $[Pb(CN)_4]^{2-}$

$+(4HCl + HNO_3)$, it is evaporated in fume hood
and diluted with 3.0 M HCl and add Hg_2Cl_2

Residue
Pd
$Hg_2^+\,Cl_2$

Filtrate
Cu^{2+}
$Hg_2^+\,Cl_2$

SCHEME 8: Systematic Analysis of Arsenic Sub-Group
II – B (Arsenic Sub-Group)

PtS_3^{2-}, AuS_2^-, MoS_4^{2-}, SnS_3^{2-}, SbS_4^{3-}, AsS_4^{3-}, (Te,Se)

H_2S is removed by neutralization with 2.0 M HCl.
The filtrate is removed

Residue
SnS_2, Sb_2S_5, As_2S_5, PtS_2, Au_2S_3, MoS_3, Te, Se

+conc. HCl, and boiled

Filtrate
$SbCl_3$, $SnCl_6^{2-}$

1. It is boiled close to dryness
+3,0 M NH_4OH, +$H_2C_2O_4$, +H_2S

2. + Metallic Fe (The black Sb is seperated from solution and Sn^{2+} stays in solution)

Residue
Sb_2S_3

Solution
Sn(IV)
$Sn(C_2O_4)_4^{4-}$

Residue
As_2S_5, PtS_2, Au_2S_3, MaS_3, Te, Se

+conc. HCl + $KClO_3$, it is boiled.

Filtrate
H_3AsO_4, $AuCl_4^-$, MoO_4^{2-}, SeO_3^{2-}, TeO_3^{2-}

Residue
K_2PtCl_6

+NH_4NO_3 + $Mg(NO_3)_2$

Filtrate
$AuCl_4^-$, MoO_4^{2-}, SeO_3^{2-}, TeO_3^{2-}

Residue
$Mg(NH_4).AsO_4.6H_2O$

Evaporated, +$H_2C_2O_4$

Filtrate
MoO_4^{2-}, SeO_3^{2-}, TeO_3^{2-}

Residue
Au

+HCl, is evaporated. If there is precipitation, it is filtered.
Na_2SO_3 is added and it is heated.

Filtrate
TeO_3^{2-}, MoO_4^{2-}

Residue
Se

It is diluted, +%10 KI,
+$Na_2S_2O_3$

Filtrate
MoO_4^{2-}

Residue
Te

+HCl, and boiled,
SO_2 evaporates, +H_2S

Residue
MoS_3

SCHEME 9: Systematic Analysis of Cations in Group III

```
Supernatant II
    │
    │ + (NH₄OH+NH₄Cl)
    │   pH 8 – 9
    │ + (NH₄)₂ S
    │
    ├──────────────→ Supernatant
    │                 Group IV and V
    ▼
Precipitate
Al(OH)₃ , Cr(OH)₃ , ZnS, FeS, MnS, CoS, NiS
    │
    │ +2N HCl
    │
    ├──────────────────────────────────→ Precipitate
    │                                      CoS, NiS
    ▼                                         │
Supernatant                                   │ Dissolve with HCl+HNO₃
Al³⁺ , Cr³⁺ , Fe²⁺ , Mn²⁺ , Zn²⁺              │  +
    │                                         │ Neutralize with Na₂CO₃
    │ +(4N NaOH+%6H₂O₂)                        │ and add dimethylglyoxime
    │                                         ▼
    ├────────────→ Precipitate        Precipitate        Supernatant
    │              Fe(OH)₃, MnO(OH)₂   Ni(OH)₂            Co(CN)₆³⁻
    │                  │               or                 or
    │                  │ Dissolve with 2N HCl  NiC₄H₇N₂O₄   Co²⁺
    │                  │ + (NH₄Cl + NH₄OH)
    │                  │
    │                  ├────→ Precipitate
    │                  │       Fe(OH)₃
    │                  │
    │                  └────→ Supernatant
    │                          MnCl₂
    ▼
Supernatant
Al(OH)₄⁻, CrO₄²⁻, Zn(OH)₄²⁻
    │
    │ +2N H₂SO₄
    │  Boiling to remove H₂O₂
    │
    ▼
Supernatant
Al³⁺ , Cr₂O₇²⁻ , Zn²⁺
    │
    │ +NH₄OH
    │
    ├────→ Precipitate
    │       Al(OH)₃
    │
    └────→ Supernatant
            CrO₄²⁻ , Zn(NH₃)₄²⁺
                │
                │ +BaCl₂ solution
                │
                ├────→ Precipitate
                │       BaCrO₄+BaSO₄
                │
                └────→ Supernatant
                        Zn(NH₃)₄²⁻
```

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SCHEME 10: Systematic Analysis of Cations in Group IV

Group III. Supernatant

1. +HCl, boiling (H_2S is removed.)
2. +(NH_4OH+NH_4Cl) pH 9
3. +(NH_4)$_2CO_3$,boiling to 80 °C

Precipitate
$BaCO_3$, $SrCO_3$, $CaCO_3$

Supernatant
Na^+, K^+, Li^+, Mg^{2+}

dil. CH_3COOH

Solution
Ba^{2+}, Sr^{2+}, Ca^{2+}

1. +CH_3COONa (pH 4.5-5)
2. +$K_2Cr_2O_7$ veya K_2CrO_4

Supernatant
Sr^{2+}, Ca^{2+}

Supernatant
Sr^{2+}, Ca^{2+}

Supernatant
Ca^{2+}

+(NH_4)$_2CO_3$

Precipitate
Yellow $SrCrO_4$

Supernatant
is removed.

Precipitate
White $CaCO_3$

+2N Na_2CO_3

Precipitate
$SrCO_3$, $CaCO_3$

dil. CH_3COOH

Solution
Ca^{2+}, Sr^{2+}

+(NH_4)$_2SO_4$

Supernatant
Ca^{2+}

(NH_4)$_2C_2O_4$

Supernatant is
removed.

Precipitate
Yellow
$BaCrO_4$

Precipitate
White $SrSO_4$
and little
amount $CaSO_4$

Precipitate
White
CaC_2O_4

SCHEME 11: Systematic Analysis of Cations in Group V

Group IV Supernatant

1. CH_3COOH, Evaporated to dryness
2. HCl, Evaporated to dryness

Precipitate
LiCl, NaCl, KCl, $MgCl_2$

+ Acetone, dioxane, amyl alcohol etc.
organic solvent

Precipitate
NaCl, KCl, $MgCl_2$

Solution
LiCl

1. Dissolved in water.
2. $H_2C_2O_4$, evaporated to dry, superheat, taken with water.

Supernatant
K^+, Na^+

The solvent is evaporated.

1. +Ethanol
2. +H_2PtCl_6 (Alcohol Solution)

Solution
Na^+

+$Mg(UO_2)_3(CH_3COO)_8$

The supernatant is removed.

Precipitate
White
LiCl

Precipitate
White
$MgCO_3$
MgO
$Mg(OH)_2$

Precipitate
White
K_2PtCl_6

Precipitate
Greenish Yellow
$NaMg(UO_2)_3(CH_3COO)_9.9H_2O$

LABORATORY PRACTICE

SCHEME 12: Systematic Analysis of HCl Group (Group I) Cations

SAMPLE SOLUTION

2N HCl

PRECIPITATE (I)
AgCl, Hg$_2$Cl$_2$, PbCl$_2$
(White) (White) (White)

SUPERNATANT
II, III, IV, V
Groups metal ions

Hot Water

SUPERNATANT
Pb^{2+}

PRECIPITATE (II)
Hg$_2$Cl$_2$, AgCl

+K$_2$Cr$_2$O$_7$ +KI
Solution

NH$_3$ (concentrated)

PbCrO$_4$ PbI$_2$
(yellow)

PRECIPITATE (III)
Hg+Hg(NH$_2$)Cl
(Black)

SUPERNATANT
Ag(NH$_3$)$_2$+Cl$^-$

HNO$_3$

AgCl
(White Precipitate)

SCHEME 13: Systematic Analysis of H₂S Group (Group II) Cations (Apply to the precipitate which is obtained from group I cations' precipitation)

HCl Precipitate + H₂S

Precipitate
(Group II Metal Precipitates)
HgS, PbS, Bi_2S_3, CuS, CdS, $As_2S_{3(5)}$, $SbS_{3(5)}$, SnS_2
black black brown yellow yellow yellow brown yellow

Solution
Group III, IV, V Metal Ions

$(NH_4)_2S_x$

Precipitate (Copper Subgroup)
HgS, PbS, Bi_2S_3, CuS, CdS
Dilute HNO_3

Precipitate (Arsenic Subgroup)
AsS_4^{3-}, SbS_4^{3-}, SnS_4^{4-}
Concentrated HCl

Precipitate
HgS

Solution
Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}

Precipitate
As_2S_3 (Soluble in $NH_3+H_2O_2$)

Solution
Sb^{3+}, Sn^{4+}

After evaporation with aqua regia, precipitate is taken.
1) It gives white precipitate with $SnCl_2$.
2) $HgCl_2+NH_3=HgNH_2Cl+Hg+NH_4Cl$
3) $Hg^{2+}+Cu=Cu^{2+}+Hg$

Evaporation with H_2SO_4, dilution with water.

Precipitate
$PbSO_4$

Solution
Bi^{3+}, Cu^{2+}, Cd^{2+}

1) Insoluble in excess H_2SO_4, Soluble in $C_4H_{12}N_2O_6$.
2) It gives yellow $PbCr_2O_7$ with $K_2Cr_2O_7$

Conc. NH3

1) It gives a yellow $(NH_4)_3[As(Mo_3O_{10})_4]$ precipitate with $(NH_4)_2MoO_4+HNO_3$.
2) It gives white $Mg(NH_4)AsO_4$ precipitate with NH_3+MgCl_2.

1) Sb^{3+} separates on Fe string.
2) It gives red Sb_2OS_2 sediment with CH_3COONH_4 and $Na_2S_2O_3$

Separation

Sb^{3+}

Sb^{4+}

1) Fluorescence
2) It gives grey precipitate with $HgCl_2$

Solution
Bi^{3+}, Cu^{2+}, Cd^{2+}

Precipitate
$Bi(OH)_3$ dissolves in HCl+NaCl and is neutralized. It gives metallic Bi(black) with $Sn(OH)_3^-$.

Solution
Blue coloured $[Cu(NH_3)_4]^{2+}$ and $[Cd(NH_3)_6]^{2+}$

$K_4[Fe(CN)_6]=Cu_2[Fe(CN)_6]$

+

KCN addition, till the blue colour disappears. H2S flow → CdS precipitate (yellow)

SCHEME 14: Systematic Analysis of (NH₄)₂S Group (Group III) Cations

To make the pH of the H_2S between 8-9, first the buffer solution is added, then Group III. cations are precipitated with $(NH_4)_2S$.

PRECIPITATE
NiS, CoS, FeS, MnS, Al(OH)₃, Cr(OH)₃, ZnS

SUPERNATANT
Group IV and V metal ions

2N HCl

PRECIPITATE
NiS, CoS

SUPERNATANT
Fe²⁺, Mn²⁺, Al³⁺, Cr³⁺, Zn²⁺
Fe²⁺ is oxidized to Fe³⁺ with HNO_3 and neutralized with Na_2CO_3 and a mixture consists of an equal volume of 30% NaOH, 3% H_2O_2 is added.

Dissolved in gold water, evaporated to dryness and dissolved in water.

The solution is separated into two portions.

Ni²⁺
- Forms pink precipitate with dimethylglyoxime.

Co²⁺
- Forms blue color in ether phase with SCN⁻.
- Forms yellow K₃[Co(NO₂)₆] precipitate with (CH₃COOH+KNO₂).

PRECIPITATE
Fe(OH)₃, Mn(OH)₂

SUPERNATANT
[Al(OH)₄]⁻, CrO₄²⁻, [Zn(OH)₃]⁻ (colorless, Yellow, Colorless) Acidified with HCl and basified with NH_3.

It is dissolved in 2N HCl and heated. The solution is separated into two portions.

Fe³⁺
- Forms red color in organic phase with KSCN.
- Forms berlin blue KFe[Fe(CN)₆] precipitate with K₄[Fe(CN)₆].

Mn²⁺
- Forms green colored Na₂MnO₄ compound with Na₂O₂ or (Na₂CO₃+KNO₃).
- Formes violet colored HMnO₄ with PbO₂+HNO₃.

PRECIPITATE
Al(OH)3

- Thenard blue is obtained with Co(NO₃)₂ .
- Gives red color with aluminum.

SUPERNATANT
CrO₄²⁻, [Zn(NH₃)₄]²⁺

BaCl₂

PRECIPITATE
BaCrO₄

SUPERNATANT
Zn²⁺

HNO₃, ether, H₂O₂

- Forms white KZn₃[Fe(CN)₆]₂ precipitate with K₄[Fe(CN)₆].
- Gives red color with dithiozone/CCl₄ solution.

Blue CrO₅ is obtained in ether phase..

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SCHEME 15: Systematic Analysis of $(NH_4)_2CO_3$ Group (Group IV) Cations and Groups without a Common Reactive Partner (Group V)

H_2S is evaporated by acidification of $(NH_4)_2S_x$ group solution with HCl. It is evaporated to remove NH_4^+ salts and evaporated to dryness with concentrated HNO_3. The precipitate is taken with water with diluted HCl and alkalized with the addition of NH_4Cl, NH_3.

Boiling with $(NH_4)_2CO_3$.

PRECIPITATE
$BaCO_3$, $SrCO_3$, $CaCO_3$

$CH_3COOH+CH_3COONa+K_2Cr_2O_7$

PRECIPITATE
$BaCrO_4$
yellow

SUPERNATANT
Sr^{2+}, Ca^{2+}

$NH_3+(NH_4)_2CO_3$

$SrCO_3$

$CaCO_3$

Diluted HCl

Sr^{2+}

- The color of the flame color is karmen red.

Mn^{2+}

- $Ca^{2+} + C_2O_4^{2-} \rightarrow CaC_2O_4$
- Brick red color is observed in flame..

SUPERNATANT
Mg^{2+}, Li^+, K^+, Na^+

PRECIPITATE
$Mg(OH)_2$

Li^+

It is observed with a carmen red color in lean flame.

SUPERNATANT
Li^+, K^+, Na^+

4.1. Groups without a Common Reactive Partner (Group V)

Cations in this group; Na^+, K^+ $Li^+, Mg^{2+}, NH_4^+, Cs^+, Fr^+$ and Rb^+ can be found in the ammonium carbonate group (Group IV) filtrate. The following are identification reactions of the most common cations:

* Mg^{2+} Ion:

1. A basic magnesium carbonate precipitate consisting of $x\,MgCO_3.y\,Mg(OH)_2$ is immediately formed when alkali carbonate is added to the solution, adding ammonium carbonate and waiting or heating. The x / y ratio is dependent on the pH of the medium, and as the pH increases, this ratio decreases. There is no precipitation in the absence of sufficient ammonium ions.

$$5\,Mg^{2+} + 5CO_3^{2-} + H_2O \longrightarrow Mg(OH)_2 \cdot 4MgCO_3 + CO_2$$

2. The sample solution is acidified with dilute HCl, then heated after adding Na_2HPO_4 solution. After adding 1 - 2 drops of phenolphthalein to the hot solution, add NH_4OH solution carefully until a pink color appears. Shiny needle-shaped $MgNH_4PO_4.6H_2O$ crystals are formed in the presence of magnesium. This reaction can be carried out next to other cations of Group V.

$$Mg^{2+} + HPO_4^{2-} + NH_4OH + 5H_2O \longrightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow$$

* Na$^+$ Ion:

1. Sodium ions present an HCl sample medium turns flame yellow.

* NH$_4^+$ Ion:

1. An alkali hydroxide solution is added to the analysis sample and heated. The resulting steam converts the color of the wet litmus paper to blue.

$$NH_4^+ + OH^- \xrightarrow{\text{ısı}} NH_3 + H_2O$$

$$NH_3 + H_2O \longrightarrow NH_4OH$$

2. Nessler's reagent is used when trace quantity of NH_4 is to be determined. Nessler's reagent is a basic solution of the potassium tetraiodomercurate and gives a yellow-brown

oxodimercuryammonia iodide precipitate with its NH_4^+ salts. Cations and acids whose hydroxides can precipitate degrade this reaction.

$$NH_4Cl + KOH \longrightarrow NH_3 + KCl + H_2O$$

$$NH_3 + 2[HgI_4]^{2-} + 3OH^- \longrightarrow [OHg_2NH_2]I \downarrow + 7I^- + 2H_2O$$

This reaction can even be used to identify ammonia in trace amounts. However, in case there is no precipitation, only the solution is colored.

Preparation of Nessler Reagent:

Saturated $HgCl_2$ solution is added to 50 mL aqueous solution of 50 g potassium iodide until insoluble HgI_2 precipitate is seen. Then 200 mL of 6 M solution is added to the mixture and completed to 1 liter volume with water. After being left to settle for a while, the clear part is taken into a dark bottle.

* K^+ Ion:

1. A sample solution acidified with acetic acid is mixed with sodium hexanitrocobalt (III) solution. A yellow-crystallized precipitate is formed if K^+ is present in the sample solution.

$$Na_3[Co(NO_2)_6] + 2K^+ \longrightarrow K_2Na[Co(NO_2)_6] + 2Na^+$$

The precipitate dissolves in mineral acids. Ammonium ions should be removed beforehand as they give a similar precipitate.

2. K^+ ions give a white crystallized precipitate with perchlorate acid. Alcohol addition to the medium reduces its solubility.

$$K^+ + HClO_4 \longrightarrow KClO_4 \downarrow + H^+$$

3. When a platinum wire is immersed in a solution containing volatile potassium salt, the platinum wire turns a flame to violet color.

* Li^+ Ion:

1. In an ammonia medium, Li^+ ion forms a white precipitate with NH_4F solution. The Group V cations except Mg^{2+} do not affect the analysis.

$$Li^+ + F^- \longrightarrow LiF \downarrow$$

2. Li$_2$CO$_3$ precipitates when heated with Na$_2$CO$_3$ solution.

$$2Li^+ + CO_3^{2-} \longrightarrow Li_2CO_3 \downarrow$$

3. Disodium hydrogen phosphate solution gives a white precipitate with Li$^+$.

$$3Li^+ + HPO_4^{2-} \longrightarrow Li_3PO_4 \downarrow + H^+$$

This precipitate is soluble in acids and in ammonium salt solutions. For this reason, the ammonium salts are firstly removed by adding NaOH to the sample solution and boiling. The solution is then diluted with HCl to make the solution weakly basic (close to neutral) and phosphate solution is added. The poorly-water soluble dilithium sodium phosphate precipitates in weak basic medium.

$$Na_2HPO_4 + 2Li^+ + OH^- \longrightarrow NaLi_2PO_4 \downarrow + H_2O + Na^+$$

The addition of a little alcohol to the medium makes the precipitation complete. Magnesium also damages the test as it will precipitate too.

4. When a platinum wire is immersed in a solvent containing volatile lithium salt, the platinum wire turns the flame reddish brown.

4.2. Ammonıum Carbonate Group (Group IV)

The filtrate of group III is acidified with HCl and boiled to remove sulfur and then pH of the solution is adjusted to approximately 9 by adding NH$_4$Cl and NH$_4$OH. Then, by adding $(NH_4)_2CO_3$ solution to the medium, Ca^{2+}, Sr^{2+} and Ba^{2+} are precipitated in the form of carbonates. The appropriate pH is 9.2. Below this pH, there is no complete precipitation and above pH 10.4, basic magnesium carbonate is also precipitated. (NH$_4$)$_2$CO$_3$ acts as a buffer solution with a pH of 9.2.

The heating of the solution to 80 ° C during precipitation ensures separation of cations in group V while ensuring the crystallization of the precipitate. In addition, the ammonium carbonate is converted to ammonium carbamate by losing water while staying in solid state.

$$(NH_4)_2CO_3 \longleftrightarrow NH_2COONH_4 + H_2O$$

Heating in an aqueous solution converts the ammonium carbamate to ammonium carbonate.

* Ba²⁺ Ion:

1. Potassium dichromate solution gives a yellow precipitate of $BaCrO_4$.

$$2Ba^{2+} + Cr_2O_7^{2-} + 3H_2O \longrightarrow 2BaCrO_4 \downarrow + 2H_3O^+$$

The sample solution is acidified with acetic acid and then buffered by the addition of excess sodium acetate. Sodium acetate keeps the pH of the solution at about 5 by neutralizing the H_3O^+ according to the above equation. Sr^{2+} and Ca^{2+} do not precipitate at this pH. $BaCrO_4$ dissolves in strong acids such as HCl, H_2SO_4 and HNO_3. The same reaction can also be done with CrO_4^{2-} solution.

2. Diluted H_2SO_4 or dissolved sulfates form white precipitates with Ba^{2+}.

$$Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4 \downarrow$$

While $BaSO_4$ is insoluble in dilute mineral acids, it dissolves in concentrated hot sulfuric acid by forming hydrogen sulfate.

$$BaSO_4 + H_2SO_4 \longrightarrow Ba(HSO_4)_2$$

3. Ammonium oxalate solution forms a white barium oxalate precipitate which is insoluble in acetic acid but soluble in mineral acids.

$$Ba^{2+} + C_2O_4^{2-} \longrightarrow BaC_2O_4 \downarrow$$

4. Volatile barium salts like $BaCl_2$ and $Ba(NO_3)_2$ turns flame to yellow-green color. For this purpose, the sample is acidified with concentrated HCl.

* Sr²⁺ Ion:

1. When saturated $CaSO_4$ or gypsum ($CaSO_4 \cdot 2H_2O$) solution is added to Sr^{2+} solution and heated, a turbidity is observed with the formation of $SrSO_4$. The same turbidity occurs immediately in the presence of Ba^{2+}.

2. Sulfate acid and water-soluble sulfate salts are form white $SrSO_4$ precipitates with Sr^{2+} solution, and the precipitate is practically insoluble in acids. Ammonium sulfate, one of the dissolved sulfates is a very suitable reactant for this reaction. Because ammonium sulfate does not precipitate with Ca^{2+} but precipitates with Sr^{2+}. $CaSO_4$ dissolves in ammonium sulfate by complex salt formation.

$$CaSO_4 + (NH_4)_2SO_4 \longrightarrow (NH_4)_2[Ca(SO_4)_2]$$

If barium ions have not been previously removed by chromate, they will interfere with the identification reaction of Sr^{2+}.

3. A drop of sample solution is placed on a filter paper. 1 drop of neutral sodium rhodizonate solution is added on it. In the presence of Sr^{2+}, a reddish-brown color is observed in the neutral medium. The color disappears when 0.5 N HCl is added dropwise. Ba^{2+} gives the same reaction but the color does not disappear with HCl. After the sample is added dropwise in the presence of Ba^{2+}, a chromate solution is dropped on the barium, then strontium is found.

4. By the addition of $(NH_4)_2C_2O_4$ solution, white crystalline SrC_2O_4 precipitates. The precipitate is slightly soluble in cold acetic acid, but soluble in mineral acids and hot acetic acid.

$$Sr^{2+} + C_2O_4^{2-} \longrightarrow SrC_2O_4 \downarrow$$

5. A red color is observed when platinum wire immersed in the salt solution of Sr^{2+} and held over a flame. This analysis is carried out by treating the water-insoluble strontium salts with HCl.

* Ca^{2+} Ion:

1. A few drops of sample solution is taken and adjusted to pH 9 by adding 1 drop of diluted NH_4OH and 1 drop of diluted NH_4Cl solutions. A few drops of saturated potassium hexacyanoferrate (II) solution is added to the solution. In the presence of Ca^{2+}, a white crystallized precipitate which is not soluble in acetic acid is formed. Sr^{2+} does not inhibit but white precipitates are formed when high concentration of Ba^{2+} is present.

$$Ca^{2+} + 2NH_4^+ + [Fe(CN)_6]^{4-} \longrightarrow Ca(NH_4)_2[Fe(CN)_6] \downarrow$$

2. The white precipitate of CaC_2O_4 is formed with $(NH_4)_2C_2O_4$ solution. This precipitate is insoluble in acetic acid while soluble in mineral acids.

$$Ca^{2+} + C_2O_4^{2-} \longrightarrow CaC_2O_4 \downarrow$$

Ba^{2+} and Sr^{2+} cations also precipitates with $C_2O_4^{2-}$. After forming sulfate salt precipitates of these ions with $(NH_4)2SO4$, Ca^{2+} can then be determined in the filtrate by adding $C_2O_4^{2-}$

3. If calcium salts treated with concentrated HCl or Ca^{2+} solution taken on a platinum wire is heated in a flame, a brick red color is seen.

FLAME TESTS

While the flame of Bunsen burner is sufficient to vaporize the alkali metals and to observe their flame colors and spectra, it does not have the same qualities for alkaline earth metals. For this reason, these substances must first be converted into volatile chloride forms in order to be able to perform qualitative analysis by spectral analysis of alkaline earth metals.

For flame tests, a 2-3 cm platinum wire piece is attached to the end of a glass rod on the burner flame. It is necessary to soak the wire with concentrated chloric acid several times and put on the flame to keep it clean. In order to obtain volatile compounds of alkali and alkaline earth metals, analysis sample is taken by a chloride wire and put on the flame.

Table 4.2 Characteristic spectral lines and flame colors of 4th and 5th Group Metals.

Elements	Color of Flame	Characteristic spectral lines (nm)
Li	Carmen red	670.8 (red), 610.3 (pale orange)
Na	Yellow	589.0 and 589.6 (double yellow lines)
K	Violet	404.4 and 404.7 (double violet lines)
		766.5 and 769.9 (double red lines)
Rb	Violet	421.0 (violet); 780.0 (red)
Cs	Blue	458.0 (blue)
Ca	Brick red	618.2 – 620.3 (red – orange band)
		555.4 (yellowish green); 422.7 (pale violet)
Sr	Red	606.0 (orange); 674.4 and 662.8 (red band);
		460.7 (blue)
Ba	Green	553.6; 534.7; 524.3; and 513.7 (green band);
		487.4 (pale blue)
Tl	Green	535.0 (green)
Cu	Green	
Pb, As, Sb	Pale blue	
V	Pale green	
Mo	Pale green	

4.3. Ammonium Sulfide Group (Group III)

In the precipitation of this group's cations (obtained from H_2S filtrate) with ammonia sulfide, the pH value must be 8.7 for a complete precipitation. For this purpose the H_2S filtrate is made weakly basic with NH_4OH. In addition, NH_4Cl is added to provide a buffered medium and to prevent the precipitation of $Mg(OH)_2$.

Some parts of the precipitate is in the form of sulfide and the other parts in hydroxide. With the exception of Zn^{2+}, cations of this group with unfilled 18 electron outer shell precipitate in the form of sulfides. Zn^{2+} which has a full 18 electron outer shell also precipitates as sulfide. Zn^{2+} also forms a transition between H_2S and $(NH_4)_2S$ groups. Cations of 3rd group which have a full outer shell of 8 electrons, precipitate in form of their hydroxides except Cr^{3+}. Actually it would be more accurate to call these precipitates hydrated oxides instead of hydroxides. For instance, $Al_2O_3.xH_2O$ instead of aluminium hydroxide, $Cr_2O_3.xH_2O$ instead of chromium hydroxide, $TiO_2.xH_2O$ instead of titanium hydroxide etc.

Hydrolysis of ammonium sulfide shows $NH_4OH + NH_4HS$ like features in water.

$$(NH_4)_2S + H_2O \longleftrightarrow NH_4OH + NH_4HS$$

Due to this phenomenon, there is no need to add buffer solution, because it acts like buffer.

* Ni^{2+} Ion

1. Ni^{2+} gives a green precipitate with ammonium hydroxide.

$$2NiSO_4 + 2NH_4OH \longrightarrow (NiOH)_2SO_4 \downarrow + (NH_4)_2SO_4$$

This precipitate gives a blue solution upon complex formation in case of excessive usage of reactants.

$$(NiOH)_2SO_4 + 12NH_4OH \longrightarrow 2[Ni(NH_3)_6]^{2+} + SO_4^{2-} + 2OH^- + 12H_2O$$

2. Ni^{2+} gives a green color $Ni(CN)_2$ precipitate with CN^-. This sediment dissolves via complexation reaction with the excess of CN^-. Adding acid to this pale yellow solution of complex precipitates Ni^{2+} as $Ni(CN)_2$ again.

$$Ni^{2+} + 2CN^- \longrightarrow Ni(CN)_2$$

$$Ni(CN)_2 + 2CN^- \longrightarrow [Ni(CN)_4]^{2-}$$

$$[Ni(CN)_4]^{2-} + 2H^+ \longrightarrow Ni(CN)_2 \downarrow + 2HCN$$

3. After adding dilute NH_4OH to make sample solution slightly basic, dimethylglyoxime solution in alcohol (Chugaev elimination) is added dropwise. In presence of Ni^{2+}, a pink-red dimethylglyoxime precipitate occurs. Sediment can be dissolved in dilute NH_4OH, mineral acids and alcohol (50% v/v alcohol solution in water). The best precipitation results can be obtained between pH 5 and 10. Acid acetate and sodium acetate buffer solution or dilute NH_4OH solution can provide this pH range. If need, the solution can be heated after addition of reactants to eliminate the excess NH_4OH. Fe^{2+} gives a red complex precipitate with Chugaev reactant which can be dissolved in water. Fe^{3+} blocks the reaction by giving a colored hydroxide precipitate at the pH of reaction. Fe^{2+} must be masked with HPO_4^{2-} or must be separated by precipitation with NH_4OH after oxidizing with H_2O_2 or HNO_3. Fe^{3+} can also be masked by addition of tartaric acid.

4. Aqueous $NaOH$ addition causes a green $Ni(OH)_2$ precipitate. This precipitate cannot be dissolved in the medium of excess reactants. It dissolves in the medium of mineral acids, NH_4OH and NH_4Cl by complexation reaction.

Oxidized to $Ni(OH)_3$ with the effects of Cl_2 and Br_2.

$$Ni^{2+} + 2OH^- \longleftrightarrow Ni(OH)_2$$

$$Ni(OH)_2 + 2HCl \longleftrightarrow NiCl_2 + 2H_2O$$

$$Ni(OH)_2 + 4NH_4OH + 2NH_4Cl \longrightarrow [Ni(NH_3)_6]Cl_2 + 6H_2O$$

$$2Ni(OH)_2 + Cl_2 + 2OH^- \longrightarrow 2Ni(OH)_3 + 2Cl^-$$

$$2Ni(OH)_2 + Br_2 + 2OH^- \longrightarrow 2Ni(OH)_3 + 2Br^-$$

5. Gives a yellow-green precipitate with $Fe(CN)_6^{4-}$. This precipitate is insoluble in acids but soluble in NH_4OH.

$$2Ni^{2+} + [Fe(CN)_6]^{4-} \longrightarrow Ni_2[Fe(CN)_6] \downarrow$$

6. Gives a greenish yellow precipitate with $Fe(CN)_6^{3-}$.

$$3Ni^{2+} + 2[Fe(CN)_6]^{3-} \longrightarrow Ni_3[Fe(CN)_6]_2 \downarrow$$

* Co^{2+}, Co^{3+}

1. Gives a black CoS_x precipitate with $(NH_4)_2S$ solution. CoS_β.

$$Co^{2+} + (NH_4)_2S \longrightarrow CoS \downarrow + 2NH_4^+$$

It is difficult to dissolve CoS in HCl. On the other hand, it is quite soluble in aqua regia and also soluble in the presence of oxidizers such as $KClO_3$, H_2O_2.

$$3CoS + 6HCl + 2HNO_3 \longrightarrow 3CoCl_2 + 2NO + 3S + 4H_2O$$
$$3CoS + 6HCl + KClO_3 \longrightarrow 3CoCl_2 + KCl + 3S + 3H_2O$$
$$CoS + 2HCl + H_2O_2 \longrightarrow CoCl_2 + S + 2H_2O$$

2. If pH is approximately set to 4 with acetic acid or citric acid after addition of excess KNO_2 to concentrated Co (II) solution, yellow crystal hexanitrocobaltate(III) precipitates are formed.

$$7NO_2 + Co^{2+} + 2H^+ + 3K^+ \longrightarrow K_3[Co(NO_2)_6] \downarrow + NO^\uparrow + H_2O$$

In dilute solutions, precipitates can be obtained only when left to stand for a while after heating. This reaction can be used to separate Co from Ni. But in the presence of Pb^{2+}, Ba^{2+}, Sr^{2+} or Ca^{2+}, nickel precipitates in form of $K_2Me^{2+}[Ni(NO_2)_6]$ yellow crystals.

3. KSCN addition to analyte solution gives a blue-water soluble complex when Co^{2+} is present.

$$Co^{2+} + 4SCN^- \longleftrightarrow [Co(SCN)_4]^{2-}$$

When the solution is diluted, its color turns pink due to the complex ions dissociation constant ($K = 1{,}0 \times 10^{-3}$). After addition of a few drops of ether or amyl alcohol, the complex crosses to the organic phase and its color turns blue.

If there is Fe^{3+} cation, it gives a red color complex with SCN^-. In identification reactions of Co^{2+}, Fe^{3+} must be masked in the form of FeF_4^{3-} or $Fe(PO_4)_2^{3-}$ by adding F^- or PO_4^{3-} to the solution.

SPOT TEST: This reaction is a more sensitive way for cobalt identification and it can be used with spot test technique. Ammonium fluoride and ammonium thiocyanate are spotted onto a filter-paper and dried. If there is cobalt in the sample, a blue spot appears when the sample is poured down this filter paper. When Co^{2+} is present with Fe^{3+}, the color first turns brown and after a while it turns blue.

4. When NH_4OH solution is slowly added to Co^{2+} solution, the basic blue cobalt salts are precipitated first, and when the reactant is continuously added, a a dirty yellow colored solution is formed upon hexamminecobalt(II) complex formation. When kept in contact with air, cobalt oxidizes and the solution's color gradually turns into red.

$$CoCl_2 + NH_4OH \longrightarrow Co(OH)Cl \downarrow + NH_4Cl$$

$$Co(OH)Cl + 7NH_4OH \longrightarrow [Co(NH_3)_6]^{2+} + NH_4Cl + 2OH^- + 6H_2O$$

$$2[Co(NH_3)_6]^{2+} + 1/2 O_2 + H_2O \longrightarrow 2[Co(NH_3)_6]^{3+} + 2OH^-$$

5. If an alkali hydroxide solution is slowly added to the Co^{2+} solution, a blue colored basic salt precipitates. If the addition of hydroxides is continued, a pink $Co(OH)_2$ precipitate forms. When the precipitate is left to open air, it slowly turns into dark brown $Co(OH)_3$.

$$CoCl_2 + NaOH \longrightarrow Co(OH)Cl \downarrow + NaCl$$

$$Co(OH)Cl + OH^- \longrightarrow Co(OH)_2 \downarrow + Cl^-$$

$$2Co(OH)_2 + 1/2 O_2 + H_2O \longrightarrow 2Co(OH)_3$$

* Fe^{3+} Ion

1. When a solution containing iron (III) cation is reacted with H2S, iron (III) is reduced to iron (II) and elemental sulfur is released.

$$2Fe^{3+} + H_2S \longrightarrow 2Fe^{2+} + S\downarrow + 2H^+$$

With ammonium sulfide, it gives FeS precipitate in the acidic medium and Fe_2S_3 precipitate in basic medium. Fe_2S_3 is soluble in HCl.

$$2Fe^{3+} + 3(NH_4)_2S \longrightarrow 2FeS\downarrow + S\downarrow + 6NH_4^+$$

2. The Fe cation gives dark red water-soluble complexes, depending on the concentration of the thiocyanate anion. When ether is added and shaken, the resulting complex crosses to the ether phase.

$$Fe^{3+} + SCN^- \longrightarrow [Fe(SCN)]^{2+}$$
$$Fe^{3+} + 2SCN^- \longrightarrow [Fe(SCN)_2]^+$$
$$Fe^{3+} + 6SCN^- \longrightarrow [Fe(SCN)_6]^{3-}$$

3. The Fe^{3+} cation gives a dark blue colored (Berlin blue) precipitate with hexacyanoferrate (II) (potassium ferrocyanide). The precipitate is insoluble in dilute HCl. It degrades by the formation of $Fe(OH)_3$ in alkali hydroxides.

$$4Fe^{3+} + 3[Fe(CN)_6]^{4-} \longrightarrow Fe_4[Fe(CN)_6]_3\downarrow$$

$$Fe_4[Fe(CN)_6]_3 + 12\,OH^- \longrightarrow 4\,Fe(OH)_3 + 3[Fe(CN)_6]^{4-}$$

4. Fe^{3+} solutions give reddish-brown $Fe(OH)^3$ precipitates with alkali bases and ammonium hydroxide. Since the precipitate does not exhibit amphoteric properties, it is insoluble in excess base and is thus separated from chromium and aluminum.

$$Fe^{3+} + 3NH_4OH \longrightarrow Fe(OH)_3 \downarrow + 3NH_4^+$$

5. With the thiosulfate anion, a red complex compound is firstly formed. However, the red color of the solution disappears with the redox reaction that causes reduction of Fe^{3+} and oxidation of $S_2O_3^{2-}$.

$$Fe^{3+} + 2Na_2S_2O_3 \longrightarrow Na[Fe(S_2O_3)_2] + 3Na^+$$
$$[Fe(S_2O_3)_2]^- \longrightarrow Fe^{3+} + 2S_2O_3^{2-}$$
$$[Fe(S_2O_3)_2]^- + Fe^{3+} \longrightarrow 2Fe^{2+} + S_4O_6^{2-}$$

6. Freshly prepared $BaCO_3$ forms $Fe(OH)_3$ precipitate with Fe^{3+}. This reaction is used to separate Fe(III) from Mn(II).

$$2\,Fe^{3+} + 3Ba\,CO_3 + 3H_2O \longrightarrow 2Fe(OH)_3 \downarrow + 3\,Ba^{2+} + 3\,CO_2$$

7. <u>Melting Method:</u> A small amount of solid sample or a few drops of sample solution is placed in a porcelain capsule. A small piece of solid Na_2O_2 is added to the sample and heated to the melting point. After heating for a while, it is left to cool. If there is iron in the sample, the residue on the porcelain capsule turns reddish-brown.

$$2Fe^{3+} + 3Na_2O_2 + 6NaOH \longrightarrow 2NaFeO_2 + 3H_2O + 5Na_2O$$

Fe^{2+} <u>Ion</u>

1. With $(NH_4)_2S$ solution, acid-soluble black FeS precipitates are formed.

$$Fe^{2+} + (NH_4)_2S \longrightarrow FeS \downarrow + 2NH_4^+$$

2. With hexacyanoferrate(III) it forms a dark-blue (Turnbull Blue) precipitate which is acid-insoluble and alkali hydroxide-degradable. The reaction was expressed in the past:

$$3Fe^{2+} + 2[Fe(CN)_6]^{3-} \longrightarrow Fe_3[Fe(CN)_6]_2 \downarrow$$

It is now expressed as:

$$Fe^{2+} + [Fe(CN)_6]^{3-} \longrightarrow Fe^{3+} + [Fe(CN)_6]^{4-}$$
$$3\,Fe(CN)_6^{4-} + 4\,Fe^{3+} \longrightarrow Fe_4[Fe(CN)_6]_3 \downarrow$$

The final precipitate has a blue color (Berlin blue). However, the precipitation of the hexacyanoferrate (III) and Fe^{2+} is a different blue from Berlin Blue. It is suggested that this difference is due to the inclusion of potassium in different amounts depending on the settling conditions.

3. It gives white $Fe(OH)_2$ precipitates with $NaOH$ and NH_4OH solutions. At the precipitation step with NH_4OH, no precipitate can be observed if there are excess amounts of NH_4^+. The $Fe(OH)_2$ precipitate first turns into green under the effect of oxygen in the air, then it turns into reddish-brown with time.

$$Fe^{2+} + 2NaOH \longrightarrow Fe(OH)_2 \downarrow + 2Na^+$$

$$Fe^{2+} + 2NH_4OH \longrightarrow Fe(OH)_2 \downarrow + 2NH_4^+$$

$$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3 \downarrow$$

4. With the addition of Na_2CO_3 solution, a white $FeCO_3$ precipitate is formed and this fades with time to brown under the effect of air oxygen.

$$Fe^{2+} + Na_2CO_3 \longrightarrow FeCO_{3\downarrow} + 2Na^+$$

$$4FeCO_3 + O_2 + 6H_2O \longrightarrow 4Fe(OH)_{3\downarrow} + 4CO_2$$

* Mn^{2+} Ion

1. With the addition of $(NH_4)_2S$ solution, Mn^{2+} gives a tan pink colored MnS precipitate which is soluble in acid acetate and dilute mineral acids. If it exposed to open-air for a long period, it is oxidized to MnO_2.

$$Mn^{2+} + (NH_4)_2S \longrightarrow MnS \downarrow + 2NH_4^+$$

$$MnS + O_2 \longrightarrow MnO_2 + S$$

2. Melting Method: A small amount of solid sample or a few drops of sample solution is placed in a porcelain capsule. A small piece of solid Na_2O_2 and NaOH are added to the sample and heated to the melting point. After heating for a while, it is left to cool. If there is $Mn(III)$ or MnO_2, the precipitate's color turns into dark green by the formation of Na_2MnO_4.

$$2MnSO_4 + 4Na_2O_2 + 4NaOH \longrightarrow 2Na_2MnO_4 + 2Na_2SO_4 + 2H_2O + 2Na_2O$$

Once the mass is dissolved in water, a careful addition of acetic acid or dilute H_2SO_4 removes MnO_2 and the solution's color becomes violet with permanganate formation.

$$3MnO_4^{2-} + 4H^+ \longrightarrow MnO_2 + 2MnO_4^- + 2H_2O$$

3. Mn^{2+} ions give poor water-soluble $MnNH_4PO_4$ precipitates with phosphate solution in ammonium medium.

$$Mn^{2+} + HPO_4^{2-} + NH_4OH \longrightarrow MnNH_4PO_4 + H_2O$$

4. If dilute HNO3 solution is added to Mn2+ solution with small amounts of PbO2 or Pb3O4 and heated, permanganate acid occurs and solution's color turns into violet. Presence of Cl^- ion has a negative effect on oxidation.

$$2Mn^{2+} + 5PbO_2 + 4H^+ \longrightarrow 2\ HMnO_4 + 5Pb^{2+} + 2H_2O$$

5. The addition of NH_4OH forms white $Mn(OH)_2$ precipitates. However, the release of NH_4^+ during the reaction makes precipitate formation (pH must be 10.83).

$$Mn^{2+} + 2NH_4OH \longrightarrow Mn(OH)_2 \downarrow + 2NH_4^+$$

When $Al^{3+}, Cr^{3+}, Fe^{3+}$ precipitate in the form of their hydroxides in the medium of NH_4OH and NH_4^+ salts, Mn^{2+} doesn't precipitate. Thus, Mn^{2+} can be separated from these cations. In NH_4OH medium, Mn^{2+} is oxidized to Mn (IV) by air oxygen to form $MnO(OH)_2$ precipitate, which makes the separation process difficult.

6. <u>Spot test:</u> After a drop of sample solution is trickled on the filter paper, the resulting stain is kept in ammonia vapor. Due to the effect of $Mn(OH)_2$'s air oxidizing to $MnO(OH)_2$ causes the spot's color to turn brown. If a drop of benzidine acetate is dropped, the stain turns into blue with the formation of benzidine blue.

$$Mn^{2+} + 2NH_4OH \longrightarrow Mn(OH)_2 + 2NH_4^+$$

$$Mn(OH)_2 + 1/2O_2 \longrightarrow MnO(OH)_2 \downarrow$$

$$MnO(OH)_2 + H_2N - C_6H_4 - C_6H_4 - NH_2 + 2CH_3COOH \longrightarrow$$

$$HN = C_6H_4 = C_6H_4 = NH + Mn^{2+} + 2CH_3COO^- + 3H_2O$$

$$HN = C_6H_4 = C_6H_4 = NH + H_2N - C_6H_4 - C_6H_4 - NH_2 + 2CH_3COOH \longrightarrow$$

$$\begin{bmatrix} HN = C_6H_4 = C_6H_4 = NH \\ H_2N - C_6H_4 - C_6H_4 - NH_2 \end{bmatrix}.2\ CH_3COOH$$

Benzidine blue.

If Co^{2+} is present in the medium, a drop of ammonium chloride solution is added to the paper after adding a drop of sample solution, then the process is continued by keeping the ammonia vapor.

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* Al³⁺ Ion

1. White gel-like $Al(OH)_3$ precipitates with $(NH_4)_2S$ solution.

$$6NH_4^+ + 3S^{2-} + 6H_2O \longrightarrow 6NH_4OH + 3H_2S$$

$$2Al^{3+} + 6NH_4OH \longrightarrow 2Al(OH)_3\downarrow + 6NH_4^+$$

2. If a drop of 2.0 M NaOH solution is added to 5 - 6 drops of sample solution, a white-colored $Al(OH)_3$ precipitate forms. Half of the suspended precipitate is taken to another test tube, then a few drops of acid is added to dissolve it by the formation of Al^{+3}. If drops of OH^- solution is added to the other half, dissolution occurs by aluminate formation.

$$Al^{3+} + H_2O \longleftrightarrow AlOH^{2+} + H^+$$

$$AlOH^2 + H_2O \longleftrightarrow Al(OH)_2^+ + H^+$$

$$Al(OH)_2^+ + H_2O \longleftrightarrow Al(OH)_3 + H^+$$

$$[Al(OH)_4] + H_2O \longleftrightarrow H[Al(OH)_4] + OH^-$$

$$H[Al(OH)_4] \longrightarrow Al(OH)_3 + H_2O$$

Between pH 5 - 9, aluminum hydroxide precipitation is complete.

At pH 10, it completely dissolves in the form of aluminate.

$$Al^{3+} + 3OH^- \longrightarrow Al(OH)_3$$

$$Al(OH)_3 + OH^- \longrightarrow [Al(OH)_4]^-$$

3. 1 - 2 drops of 0.01% aluminon solution is added to the sample solution containing a small amount of acetic acid and it is heated in a water bath. NH_4OH and 1 - 2 drops of $(NH_4)_2CO_3$ are added until the distinct ammonia odor is smelled. The formation of dark red precipitate indicates the presence of Al^{3+} in the sample.

* Cr^{3+} Ion

1. Chromium (III) gives a greenish $Cr(OH)_3$ precipitates with $(NH_4)_2S$ solution.

$$(NH_4)_2S + 2H_2O \longleftrightarrow 2NH_4OH + H_2S$$

$$Cr^{3+} + 3NH_4OH \longrightarrow Cr(OH)_{3\downarrow} + 3NH_4^+$$

2. The alkaline hydroxide solution forms a $Cr(OH)_3$ precipitate which is soluble in excess reagent.

$$Cr(OH)_3 + OH^- \longrightarrow [Cr(OH)_4]^-$$

The following equilibrium occurs in an aqueous solution because of the amphoteric property of $Cr(OH)_3$.

$$H^+ + H_2CrO_3 \longleftrightarrow H_3CrO_3 \longleftrightarrow Cr(OH)_3 \longleftrightarrow Cr^{3+} + 3OH^-$$

3. Oxidation of chromium (III) cation to chromium (VI):

Oxidation in basic medium:

In the basic medium, chromium (III) is present in the form of chromite (CrO_2^-), and H_2O_2 or Na_2O_2 are usually used as oxidizing agents.

a) 4 - 5 drops of 2.0 M NaOH and 2 - 3 drops of 3% H_2O_2 are added to 2 - 3 drops of sample solution and heated for a few minutes. Due to the formation of chromate anions, the green color of the solution turns yellow.

$$2CrO_2^- + 3H_2O_2 + 2OH^- \longrightarrow 2CrO_4^{2-} + 4H_2O$$

b) Flux Test: A small amount of sample or a few drops of sample solution is taken to a porcelain capsule. A small amount of Na_2O_2 and NaOH are added and is heated till it is melted. After heating for a while, it is left to cool. If the sample contains chromium (III), the material in the porcelain turns yellow due to the formation of CrO_4^{2-} anion.

$$Cr_2(SO_4)_3 + 3Na_2O_2 + 4NaOH \longrightarrow 2Na_2CrO_4 + 3Na_2SO_4 + 2H_2O$$

c) In a basic medium, the oxidation can also be achieved with bromine or chlorine water.

$$2CrO_2^- + 3Br_2 + 8OH^- \longrightarrow 2CrO_4^{2-} + 6Br^- + 4H_2O$$

Oxidation in acidic medium

It is usually done with strong oxidants such as $KMnO_4, (NH_4)_2S_2O_8$.

a) A drop of 2.0 M H_2SO_4 is added to 5 - 6 drops of $(NH_4)_2S_2O_8$ solution, then silver salt is added as a catalyst. A portion of this solution is added to $Cr_2(SO_4)_3$ or $Cr(NO_3)_3$ solution and heated. Due to the $Cr_2O_7^{2-}$ formation, the solution becomes yellow. (Since the oxidizing agents will oxidize Cl^- anion to Cl_2, $CrCl_3$ solution is not preferred.)

$$2Cr^{3+} + S_2O_8^{2-} + 17H_2O \longrightarrow Cr_2O_7^{2-} + 2SO_4^{2-} + 14H^+$$

b) If MnO_4^- is added to the Cr^{3+} solution and heated, turbidity due to the formation of $MnO(OH)_2$ disappears immediately, and the solution becomes yellow due to the $Cr_2O_7^{2-}$ ion.

$$10Cr^{3+} + 6MnO_4^- + 11H_2O \longrightarrow 5Cr_2O_7^{2-} + 6Mn^{2+} + 22H^+$$

4. Reduction of chromium (VI) to chromium (III):

It is done using reducing agents such as $Na_2SO_3, H_2S,$ ethyl alcohol, Fe^{2+}.

A few drops of Na_2SO_3 solution is added to dichromate solution, and if acidified by H_2SO_4, Cr^{3+} occurs and the yellow color of the solution turns green.

$$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$$

The identification of $CrO_4^{2-}, Cr_2O_7^{2-}$ anions can be found in the Anion Analysis Section.

* Zn^{2+} Ion

1. With $(NH_4)_2S$ solution, white-colored, acid soluble ZnS precipitates are formed.

$$Zn^{2+} + (NH_4)_2S \longrightarrow ZnS\downarrow + 2NH_4^+$$

$$ZnS + 2H^+ \longrightarrow Zn^{2+} + H_2S\uparrow$$

2. The zinc-containing solution gives gelatinous zinc hydroxide precipitate with alkaline bases.

$$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2 \downarrow (white)$$

This precipitate dissolves the excess of NH_4OH by forming hexamine or tetraamine complex.

$$Zn(OH)_2 + 4NH_4OH \longrightarrow [Zn(NH_3)_4]^{2+} + 2OH^- + 4H_2O$$

3. With potassium hexacyanoferrate (II), white zinc potassium hexacyanoferrate (II) precipitate is obtained. Utilizing this reaction, Zn^{2+} can be separated from Al^{3+} which does not precipitate with hexacyanoferrate.

$$3Zn^{2+} + 2K^+ + 2[Fe(CN)_6]^{4-} \longrightarrow K_2Zn_3[Fe(CN)_6]_2 \downarrow$$

4. With potassium hexacyanoferrate (III), a yellow-brown precipitate is formed. This precipitate is also soluble in HCl and NH_4OH.

$$3Zn^{2+} + 2K_3[Fe(CN)_6] \longrightarrow Zn_3 [Fe(CN)_6]_2 \downarrow + 6 K^+$$

4.4. Hydrogen Sulfide Group (Group II)

If needed, NH_4OH is added to group I filtrates to adjust the solution to pH five and cations in this group are then precipitated with H_2S. Depending on the properties of the sulfides, cations are examined under two groups.

A. Copper Subgroup

Pt(IV), Au(III), $Hg^{2+}, Pb^{2+}, Bi^{3+}, Cd^{2+}, Pd^{2+}, Cu^{2+}$ cations are present in this group. The oxides corresponding to their sulfides show basic properties.

B. Arsenic Subgroup

Sb(III), Sb(V), Sn^{2+}, Sn(IV), As(III), As(V), Pt(IV), Au(III), Mo(VI) cations and Se(IV), Te(IV) are present in this group. The oxides corresponding to their sulfides show acidic properties. Their sulfides dissolve by giving thio-salts in ammonium polysulfide, ammonium sulfide, and alkaline sulfide solutions and by giving oxy-thio salt in alkaline hydroxides. Ammonium polysulfide is preferred because of its oxidizing property. Thus, tin-sulfide which

can only be dissolved by oxidation also enters the solution. If the thio salts solutions are acidified, the sulfides in the high oxidation step are separated by precipitating again.

Note: Elements given their valances as Pt(IV), As(III), Mo(VI) etc. are found as complex anions and as Hg^{2+}, Cu^{2+}, Pb^{2+} etc. are found as cations in the solution.

Copper Subgroup Ions:

Pt(IV) Ion

It is in the form of $[PtCl_6]^{2-}$ in solution.

1. Black colored PtS_2 precipitates are formed with H_2S in an acidic medium. When the PtS_2 precipitate is heated after adding concentrated HCl and Br_2, it dissolves in the form of hexachloroplatinate acid.

$$PtS_2 + 6HCl + 2Br_2 \longrightarrow H_2[PtCl_6] + 4HBr + 2S$$

KCl is added to the solution, and if concentrated by evaporating, yields yellow colored crystallized potassium hexachloroplatinate precipitate.

$$2KCl + [H_2PtCl_6] \longrightarrow K_2[PtCl_6] \downarrow + 2HCl$$

2. With NH_4OH solution, yellow colored ammonium hexachloroplatinate precipitate is obtained. If the precipitate is heated, it decomposes by giving a black precipitate of Pt.

$$2NH_4^+ + [PtCl_6]^{2-} \longrightarrow (NH_4)_2[PtCl_6]$$
$$(NH_4)_2[PtCl_6] \longrightarrow Pt \downarrow + 2NH_3 + 2HCl + 2Cl_2$$

3. If $SnCl_2$ is added to $PtCl_6^{2-}$ solution, colloidal platinum which changes from yellow to red is formed.

$$[PtCl_6]^{2-} + 2Sn^{2+} \longrightarrow Pt \downarrow + 2Sn^{4+} + 6Cl^-$$

4. When the sample solution is acidified with HCl and then Zn grain is added, black colored Pt precipitate is formed. Pt is insoluble in mineral acids, but soluble in gold water.

$$[PtCl_6]^{2-} + 2Zn \longrightarrow Pt + 2Zn^{2+} + 6Cl^-$$

5. With $AgNO_3$ solution yellow colored $Ag_2[PtCl_6]$ precipitate which is soluble in KCN and also slightly soluble in NH_4OH is formed.

$$2Ag^+ + [PtCl_6]^{2-} \longrightarrow Ag_2[PtCl_6]\downarrow$$

6. If a drop of 10% KI is added to the $PtCl_6^{4-}$ containing solution, PtI_6^{2-} is produced and the solution becomes reddish–brown. Black precipitates of PtI_4 are formed in an excess of KI or upon heating.

$$PtCl_6^{2-} + 6I^- \longrightarrow [PtI_6]^{2-} + 6Cl^-$$

$$[PtI_6]^{2-} \longrightarrow PtI_4 \downarrow + 2I^-$$

Au(III) Ion

It is in the form of $[AuCl_4]^-$ in solution.

1. In acidic medium, black Au_2S_3 precipitate are formed with H_2S. Au_2S_3 immediately turns into Au_2S in the cold and also turns into Au under heat. Au_2S dissolves by giving ammonium polysulfide thiolate anion.

$$2H[AuCl_4] + 3H_2S \longrightarrow Au_2S_3 \downarrow + 8HCl$$

$$Au_2S_3 \longrightarrow Au_2S + 2S \downarrow$$

$$Au_2S + 2(NH_4)_2S_2 \longrightarrow 2NH_4AuS_2 + (NH_4)_2S$$

2. It is reduced to metallic gold by the effect of oxalic acid.

$$2H[AuCl_4] + 3H_2C_2O_4 \longrightarrow 2Au \downarrow + 6CO_2 + 8HCl$$

The reduction of $[AuCl_4]^-$ can also be performed with SO_3^{2-}, SnCl$_2$, Sn, Zn, and Fe. The resulting colloidal gold, exhibits various colors ranging from yellow to violet, depending on grain size.

$$2H[AuCl_4] + 3Zn \longrightarrow 2Au + 3ZnCl_2 + 2HCl$$

$$2H[AuCl_4] + 3SnCl_2 + 9H_2O \longrightarrow 3SnO_2 + 2Au + 14HCl + 3H_2O$$

* Hg^{2+} Ion

1. In an acidic medium, a white precipitate with H$_2$S, initially in the form of 2HgS.HgCl2 is converted to a black HgS after going through yellow-red and brown, if the addition of H$_2$S is continued.
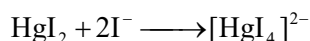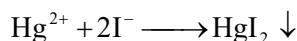
$$3HgCl_2 + 2H_2S \longrightarrow 2HgS.HgCl_2 \downarrow + 4HCl$$

$$2HgS . HgCl_2 + H_2S \longrightarrow 3HgS \downarrow + 2HCl$$

The HgS precipitate is insoluble in HCl and dilute HNO$_3$. With the effect of concentrated HNO$_3$, Hg(NO$_3$)$_2$.2HgS is formed. It dissolves under the influence of an oxidizing agent such as KClO$_3$ in combination of aqua regia or HCl. HgS also dissolves in concentrated HCl medium containing KI.

$$3HgS + 4HNO_3 \longrightarrow Hg(NO_3)_2 . 2HgS + S + 2NO_2 \uparrow + 2H_2O$$

$$3HgS + 6HCl + 2HNO_3 \longrightarrow 3HgCl_2 + 2NO \uparrow + 3S + 4H_2O$$

$$3HgS + 6HCl + KClO_3 \longrightarrow 3HgCl_2 + 3S + KCl + 3H_2O$$

$$HgS + 2H^+ + 4I^- \longrightarrow [HgI_4]^{2-} + H_2S$$

HgS, constitutes a transition between copper subgroup and arsenic subgroup cations sulfides. It is insoluble in ammonium polysulfide and ammonium sulfide but it dissolves by giving thiosphosphate in alkaline sulfide solutions with a higher percentage of ionization. In the presence of ammonium salts, this dissolution does not occur. HgS is re-precipitated by diluting thio salts.

$$HgS + Na_2S \longrightarrow Na_2HgS_2$$

$$[HgS_2]^{2-} + NH_4^+ + H_2O \longrightarrow HgS \downarrow + HS^- + NH_4OH$$

$$Na_2HgS_2 + H_2O \longrightarrow HgS \downarrow + NaHS + NaOH$$

2. In excess reagent and with KI solution, a red colored HgI$_2$ precipitate is obtained.

$$Hg^{2+} + 2I^- \longrightarrow HgI_2 \downarrow$$

$$HgI_2 + 2I^- \longrightarrow [HgI_4]^{2-}$$

3. With $K_2CrO_4, K_2Cr_2O_7$ solutions, a yellow $HgCrO_4$ precipitate is obtained.

$$Hg^{2+} + CrO_4^{2-} \longrightarrow HgCrO_4 \downarrow$$

$$2Hg^{2+} + Cr_2O_7^{2-} + H_2O \longrightarrow 2HgCrO_4 \downarrow + 2H^+$$

4. If Hg^{2+} is treated with $SnCl_2$ solution, white Hg_2Cl_2 precipitates first. When the addition of reagent is continued, the metallic mercury is removed and the color of the precipitate turns black.
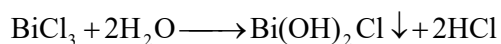
$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 \downarrow + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg \downarrow + SnCl_4$$

5. Metallic mercury is formed by the reducing effect of metals such as aluminum, zinc, iron etc.

$$Hg_2^{2+} + Zn \longrightarrow 2Hg \downarrow + Zn^{2+}$$

$$Hg^{2+} + Fe \longrightarrow Hg \downarrow + Fe^{2+}$$

* Bi^{3+} Ion

1. Bismuth salts are hydrolyzed in an acid-free aqueous medium and white colored basic salt precipitates. For example, bismuth chloride forms bismuth dihydoxychloride.

$$BiCl_3 + 2H_2O \longrightarrow Bi(OH)_2Cl \downarrow + 2HCl$$

Unstable hydroxyl salts turn into oxy salts.

$$Bi(OH)_2Cl \longrightarrow BiOCl + H_2O$$

The basic salt is dissolved by adding acid to the medium.

$$BiOCl + 2H^+ \longrightarrow Bi^{3+} + Cl^- + H_2O$$

2. In an acidic medium, a brownish – black sulfide precipitate is formed with H_2S.

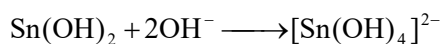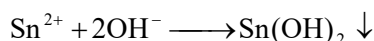$$2Bi^{3+} + 3H_2S \longrightarrow Bi_2S_3 \downarrow + 6H^+$$

3. Bismuth hydroxide, which is precipitated with NH₄OH rapidly transforms into basic bismuth oxide. In the excess of NH_4OH, Bi^{3+} ion can be separated from Cd^{2+}, Pd^{2+}, and Cu^{2+} on the principle that Bi^{3+} ions dissolves in basic oxides, while Cd^{2+}, Pd^{2+} and Cu^{2+} ions dissolve as $[Cd(NH_3)_4]^{2+}$ $[Pd(NH_3)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$ complexes.

$$Bi^{3+} + 3OH^- \longrightarrow Bi(OH)_3 \downarrow$$

$$Bi(OH)_3 \longrightarrow BiO(OH) \downarrow + H_2O$$

4. If the bismuth-containing sample solution is added to stannite solution, a black metallic bismuth precipitate forms.

$$Bi^{3+} + 3OH^- \longrightarrow Bi(OH)_3 \downarrow$$

$$2Bi(OH)_3 + 3[Sn(OH)_4]^{2-} \longrightarrow 2Bi \downarrow + 3[Sn(OH)_6]^{2-}$$
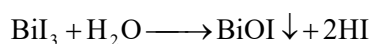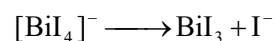
Preparation of sodium stannite solution: Sodium hydroxide is added drop by drop to Sn^{2+} solution. Sodium hydroxide is continually added until the $Sn(OH)_2$ precipitate dissolves.

$$Sn^{2+} + 2OH^- \longrightarrow Sn(OH)_2 \downarrow$$

$$Sn(OH)_2 + 2OH^- \longrightarrow [Sn(OH)_4]^{2-}$$

5. When concentrated potassium iodide solution is added to acidic bismuth solution, black colored bismuth iodide precipitates. In excess of reagent, the precipitate dissolves by giving orange colored $[BiI_4]^-$ complex.

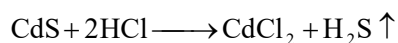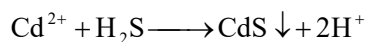$$Bi^{3+} + 3I^- \longrightarrow BiI_3$$

$$BiI_3 + I^- \longrightarrow [BiI_4]^-$$

If the solution containing $[BiI_4]^-$ complex is diluted again, BiI_3 is precipitated. If it is more diluted, the orange colored bismuth oxy iodide is precipitated.
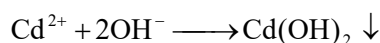
$$[BiI_4]^- \longrightarrow BiI_3 + I^-$$

$$BiI_3 + H_2O \longrightarrow BiOI \downarrow + 2HI$$
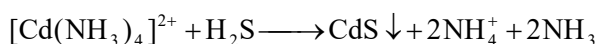
*Cd^{2+} Ion

1. In an acidic medium, the addition of H_2S results in the formation of yellow colored CdS precipitates. The precipitate is dissolved in dilute HCl, H_2SO_4 and dilute HNO_3 by the separation of S.
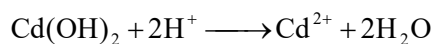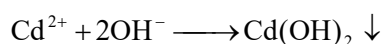
$$Cd^{2+} + H_2S \longrightarrow CdS \downarrow + 2H^+$$

$$CdS + 2HCl \longrightarrow CdCl_2 + H_2S \uparrow$$

$$CdS + 8HNO_3 \longrightarrow 3Cd(NO_3)_2 + 2NO \uparrow + 3S \downarrow + 4H_2O$$

2. White Cd(OH)$_2$ precipitates from the reaction with NH_4OH dissolves by giving a colorless tetraamine complex in excess of reagent.
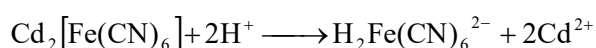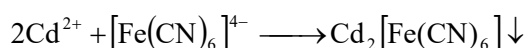
$$Cd^{2+} + 2OH^- \longrightarrow Cd(OH)_2 \downarrow$$

$$Cd(OH)_2 + 4NH_4OH \longrightarrow [Cd(NH_3)_4]^{2+} + 2OH^- + 4H_2O$$

If H_2S is added into the cadmium tetraamine complex solution, CdS precipitates again.

$$[Cd(NH_3)_4]^{2+} + H_2S \longrightarrow CdS \downarrow + 2NH_4^+ + 2NH_3$$

3. The Cd(OH)$_2$ precipitate formed by alkali hydroxide solutions dissolves in acids and NH4OH solutions.

$$Cd^{2+} + 2OH^- \longrightarrow Cd(OH)_2 \downarrow$$

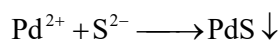$$Cd(OH)_2 + 2H^+ \longrightarrow Cd^{2+} + 2H_2O$$

4. When 1-2 drops of 0.1 M potassium ferrocyanide are added to 3-4 drops of the Cd^{2+} solution, a white-cream precipitate is formed. The precipitate dissolves when treated with dilute HCl.
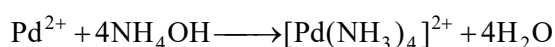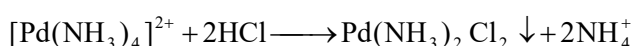
$$2Cd^{2+} + [Fe(CN)_6]^{4-} \longrightarrow Cd_2[Fe(CN)_6] \downarrow$$

$$Cd_2[Fe(CN)_6] + 2H^+ \longrightarrow H_2Fe(CN)_6^{2-} + 2Cd^{2+}$$

<u>*Pd^{2+} Ion</u>

1. In an acidic medium, a black colored PdS precipitate is formed with the addition of H$_2$S.

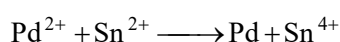$$Pd^{2+} + S^{2-} \longrightarrow PdS \downarrow$$

2. When NH$_4$OH is added drop by drop to the palladium solution, a red colored precipitate is formed. If reagent addition continues, palladium dissolves by the formation of tetraamine complex.

$$Pd^{2+} + 4NH_4OH \longrightarrow [Pd(NH_3)_4]^{2+} + 4H_2O$$

If diluted HCl solution is added carefully into the tetraamine solution, crystallized yellow precipitates are formed.

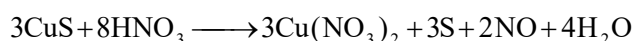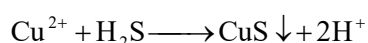$$[Pd(NH_3)_4]^{2+} + 2HCl \longrightarrow Pd(NH_3)_2 Cl_2 \downarrow + 2NH_4^+$$

3. It is reduced under the influence of Hg$_2$Cl$_2$ or SnCl$_2$ to form brown Pd suspension.

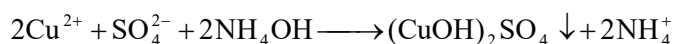$$Pd^{2+} + Sn^{2+} \longrightarrow Pd + Sn^{4+}$$

<u>*Cu^{2+} Ion</u>

1. Black colored CuS precipitate is formed with H$_2$S in acidic medium, and it dissolves in diluted HNO$_3$.

$$Cu^{2+} + H_2S \longrightarrow CuS \downarrow + 2H^+$$

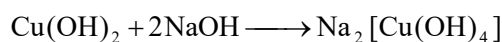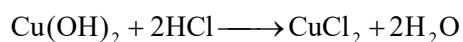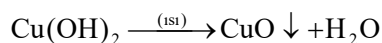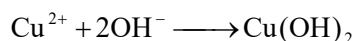$$3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 3S + 2NO + 4H_2O$$

2. When a small amount of NH$_4$OH is added to the Cu^{2+} solution, a greenish basic salt precipitates. This precipitate dissolves by giving a dark blue tetraamine complex in excess of reagent (pH>9).

$$2Cu^{2+} + SO_4^{2-} + 2NH_4OH \longrightarrow (CuOH)_2 SO_4 \downarrow + 2NH_4^+$$

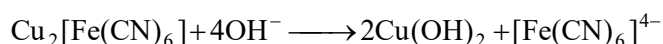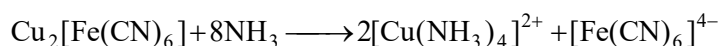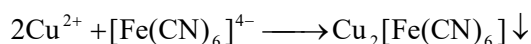$$(CuOH)_2 SO_4 + 8NH_4OH \longrightarrow 2[Cu(NH_3)_4]^{2+} + SO_4^{2-} + 2OH^- + 8H_2O$$

3. Blue colored copper hydroxide precipitates with alkali hydroxide solutions. When the precipitate is heated, black copper oxide is obtained. Copper hydroxide has weak amphoteric
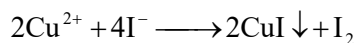
properties. For this reason, as in acids, it dissolves, especially when it is heated by giving a complex in excess of alkali hydroxide.
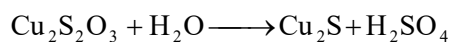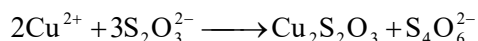
$$Cu^{2+} + 2OH^- \longrightarrow Cu(OH)_2$$

$$Cu(OH)_2 \xrightarrow{(\text{ısı})} CuO \downarrow + H_2O$$

$$Cu(OH)_2 + 2HCl \longrightarrow CuCl_2 + 2H_2O$$

$$Cu(OH)_2 + 2NaOH \longrightarrow Na_2[Cu(OH)_4]$$

4. A brown copper ferrocyanide precipitate is obtained with potassium ferrocyanide solution. The precipitate does not dissolve in acids but dissolves in NH_4OH with the formation tetraamine complex, and degrades under the influence of alkali hydroxides.

$$2Cu^{2+} + [Fe(CN)_6]^{4-} \longrightarrow Cu_2[Fe(CN)_6] \downarrow$$

$$Cu_2[Fe(CN)_6] + 8NH_3 \longrightarrow 2[Cu(NH_3)_4]^{2+} + [Fe(CN)_6]^{4-}$$

$$Cu_2[Fe(CN)_6] + 4OH^- \longrightarrow 2Cu(OH)_2 + [Fe(CN)_6]^{4-}$$

5. White CuI precipitates are formed with KI solution resulting in the separation of I_2.

$$2Cu^{2+} + 4I^- \longrightarrow 2CuI \downarrow + I_2$$

6. If thiosulfate solution is added to a blue acidified Cu^{2+} solution, Cu^{2+} reduces to Cu+ and the solution's color disappears. If this solution is heated, dark brown copper I sulfide precipitates.

$$2Cu^{2+} + 3S_2O_3^{2-} \longrightarrow Cu_2S_2O_3 + S_4O_6^{2-}$$

$$Cu_2S_2O_3 + H_2O \longrightarrow Cu_2S + H_2SO_4$$

When thiosulfate solution is added to Cd^{2+} and heated, CdS does not form. So this reaction is used for distinguishing Cu^{2+} from Cd^{2+}.

*Pb^{2+} Ion

1. White $PbCl_2$ precipitates are formed with dilute HCl and soluble chlorides. Since $PbCl_2$ dissolves to a certain extent in water, the Pb^{2+} ion is present in both the HCl and H_2S groups. $PbCl_2$ dissolves in hot water and concentrated HCl.

$$Pb^{2+} + 2Cl^- \longrightarrow PbCl_2$$

$$PbCl_2 + 2HCl \longrightarrow H_2[PbCl_4]$$

2. White crystallized PbSO$_4$ precipitates are formed with dilute sulfuric acid. PbSO$_4$ does not dissolve in dilute acids. It dissolves in concentrated HCl, concentrated H$_2$SO$_4$, alkali acetate, tartrate and ammonium citrate solution by heating.

$$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$$

$$PbSO_4 + H_2SO_4 \longrightarrow Pb(HSO_4)_2$$

$$PbSO_4 + AHCl \longrightarrow H_2[PbCl_4] + H_2SO_4$$

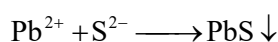$$2PbSO_4 + 2CH_3COO^- \longrightarrow Pb(CH_3COO)_2 . PbSO_4 + SO_4^{2-}$$

$$PbSO_4 + [C_4H_2O_6]^{4-} \longrightarrow [PbC_4H_2O_6]^{2-} + SO_4^{2-} + 2H^+$$

3. Black PbS precipitates are formed with H$_2$S in acidic, basic and neutral media.

$$Pb^{2+} + S^{2-} \longrightarrow PbS \downarrow$$

4. Yellow PbI$_2$ precipitates formed with I$^-$ ion dissolves in hot water by complex formation in excess reagent. When the yellow precipitate formed by the addition of KI solution to sample solution including Pb^{2+} is heated and quickly cooled, bright yellow PbI$_2$ crystals are formed and can be easily recognized.

$$Pb^{2+} + 2I^- \longrightarrow PbI_2 \downarrow$$

$$PbI_2 + 2I^- \longrightarrow [PbI_4]^{2-}$$

5. With chromate and dichromate solutions, yellow lead chromate precipitates are formed. The precipitate does not dissolve in 2.0 M HNO$_3$, CH$_3$COOH or NH$_4$OH, but dissolves in 3.0 M HNO$_3$ and alkali hydroxides.

$$Pb^{2+} + CrO_4^{2-} \longrightarrow PbCrO_4 \downarrow$$

$$2Pb^{2+} + Cr_2O_7^{2-} + H_2O \longrightarrow 2PbCrO_4 \downarrow + 2H^+$$

$$2PbCrO_4 + 2H^+ \longrightarrow 2Pb^{2+} + Cr_2O_7^{2-} + H_2O$$

$$PbCrO_4 + 4OH^- \longrightarrow [Pb(OH)_4]^{2-} + CrO_4^{2-}$$

6. Reaction with sodium thiosulfate solution gives white precipitate which is soluble in excess of reagent.

$$Pb^{2+} + S_2O_3^{2-} \longrightarrow PbS_2O_3 \downarrow$$

$$PbS_2O_3 + 2S_2O_3^{2-} \longrightarrow [Pb(S_2O_3)_3]^{4-}$$

If the final solution is heated, black PbS precipitates in acidic medium or in a medium with NH$_4$Cl.

$$[Pb(S_2O_3)_3]^{4-} + 2H^+ \longrightarrow PbS \downarrow + 2S + 2SO_2 + SO_4^{2-} + H_2O$$

Determination of Arsenic Subgroup Ions:

* Sb(III) Ion

1. Antimony is found in the form of $SbCl_6^{3-}$ in semi-concentrated HCl medium. If this solution is diluted, basic salt precipitates by hydrolysis of antimony. For example, if aqueous SbCl$_3$ solution is diluted, it results in the hydrolysis of antimony oxychloride precipitates. In excess HCl, the basic salt dissolves by heating. It also dissolves in tartaric acid by forming a complex.

$$H_3[SbCl_6] + H_2O \longrightarrow SbOCl + 5HCl$$

$$SbOCl + 2H^+ \longrightarrow Sb^{3+} + Cl^- + H_2O$$

When tartrate ion is added into the medium, precipitation is not observed because of water soluble antimony tartrate formation.

$$SbOCl + H_2C_4H_4O_6 \longrightarrow (SbO)HC_4H_4O_6 + HCl$$

2. In an acidic medium, orange colored Sb$_2$S$_3$ precipitates are formed with H$_2$S. The precipitate dissolves in concentrated HCl. It dissolves by the formation of thioantimonite in alkali sulfide and ammonium sulfide solutions, and thioantimonate in ammonium polysulfide. When thioantimonite is acidified, Sb$_2$S$_3$ precipitates again. Sb$_2$S$_3$ does not dissolve in NH$_4$OH, (NH$_4$)$_2$ and CO$_3$ solutions. It gives hardly soluble Sb$_2$O$_5$.nH$_2$O complex in the presence of concentrated HNO$_3$.

$$2H_3[SbCl_6] + 3H_2S \longrightarrow Sb_2S_3 \downarrow + 12HCl$$

$$Sb_2S_3 + 3Na_2S \longrightarrow 2Na_3SbS_3$$

$$Sb_2S_3 + 3(NH_4)_2S \longrightarrow 2(NH_4)_3SbS_3$$

$$Sb_2S_3 + 3(NH_4)_2S_2 \longrightarrow 2(NH_4)_3SbS_4 + S$$

$$2(NH_4)_3SbS_3 + 6HCl \longrightarrow Sb_2S_3 \downarrow + 3H_2S + 6NH_4Cl$$

$$nH_2O + Sb_2S_3 + 10HNO_3 \longrightarrow Sb_2O_5 \cdot (n+5)H_2O + 3S + 10NO_2$$

3. In the presence of alkali hydroxide and ammonium hydroxide solutions, white colored antimonic acid precipitates. This compound which shows amphoteric properties dissolves in strong acids and alkali hydroxides.

$$[SbCl_6]^{3-} + 3OH^- \longrightarrow HSbO_2 + 6Cl^- + H_2O$$

$$HSbO_2 + 3H^+ + 6Cl^- \longrightarrow [SbCl_6]^{3-} + 2H_2O$$

$$HSbO_2 + OH^- \longrightarrow SbO_2^- + H_2O$$

4. When weakly acidic Sb (III) solution, is heated after adding thiosulfate solution, a red colored antimony sulfoxide precipitates.

$$2H_3[SbCl_6] + 2S_2O_3^{2-} + 3H_2O \longrightarrow Sb_2OS_2 \downarrow + 2SO_4^{2-} + 12HCl$$

Antimony (III) sulfur precipitates in moderately acidic medium.

$$2H_3[SbCl_6] + 3S_2O_3^{2-} + 3H_2O \xrightarrow{(H^+)} Sb_2S_3 \downarrow + 3SO_4^{2-} + 12HCl$$

5. Sb(III) ion oxidizes to Sb(V) with permanganate, dichromate and bromate in acidic medium, with permanganate and dichromate in neutral medium, and with permanganate in basic medium.

$$3H_3[SbCl_6] + BrO_3^- \longrightarrow 3H[SbCl_6] + Br^- + 3H_2O$$

6. In acidic medium, Sb(III) ion reduces to elemental form of antimony as a results of reaction with Fe, Al, Mg, Zn, Sn etc.

$$2H_3[SbCl_6] + 3Fe \longrightarrow 2Sb + 3FeCl_2 + 6HCl$$

Metals which have smaller standard reduction potential than antimony such as Zn, Mg, Al form hydrogen antimony with antimony (III) ion in strongly acidic medium.

$$H_3[SbCl_6] + 3Zn \xrightarrow{(H^+)} H_3Sb + 3ZnCl_2$$

When the resulting H_3Sb gas is heated, it decomposes to elemental antimony and hydrogen. The product forms a mirror on the cold porcelain or glass surface.

$$2H_3Sb \xrightarrow{(ısı)} 2Sb + 3H_2$$

Sb(V) Ion

1. Salts of Antimony (V) are hydrolyzed in dilute aqueous solutions and white colored basic salt precipitates. This precipitate dissolves by heating in excess HCl.

$$H[SbCl_6] + 2H_2O \longleftrightarrow SbO_2Cl + 5HCl$$

2. In an acidic medium, Sb_2S_3 precipitates in the presence of H_2S by decomposition of Sb_2S_5 or S. Sb_2S_5 precipitate; $(NH_4)_2S$ is reduced to Sb (III) together with sulfur removal in concentrated HCl, by giving thioantimonate in Na_2S and NaOH solutions.

$$2H[SbCl_6] + 5H_2S \longrightarrow Sb_2S_5 \downarrow + 12HCl$$

$$2Sb_2S_5 + 12NaOH \longrightarrow Na_3SbS_4 + 3Na_3SbO_2S_2 + 6H_2O$$

$$Sb_2S_5 + 6HCl \longrightarrow 2SbCl_3 + 3H_2S + 2S$$

When thioantimonate is acidified with HCl, Sb_2S_5 precipitate is obtained again.

$$2(NH_4)_3SbS_4 + 6HCl \longrightarrow Sb_2S_5 \downarrow + 3H_2S \uparrow + 6NH_4Cl$$

3. White metaantimonate acid precipitates with the careful addition of alkaline hydroxide or NH_4OH.

$$H[SbCl_6] + 6OH^- \longrightarrow HSbO_3 + 6Cl^- + 3H_2O$$

4. The Sb (V) ion is reduced by metallic Sn, Zn, Mg, Al and Fe in an acidic medium as described for the Sb (III) ion.

* Sn(II) Ion

1. It gives a brown SnS precipitate with H_2S in an acidic medium. SnS dissolves in concentrated HCl solution and in ammonium polysulfide. In alkali hydroxide and alkali sulfide solutions, it dissolves in the presence of oxidizing agents such as hydrogen peroxide etc. (difference between arsenic and antimony).

$$Sn^{2+} + H_2S \longrightarrow 2H^+ + SnS \downarrow$$

$$SnS + (NH_4)_2S_2 \longrightarrow (NH_4)_2SnS_3$$

$$3SnS + 6NaOH + 3H_2O_2 \longrightarrow Na_2SnS_3 + 2Na_2[Sn(OH)_6]$$

2. White colored $Sn(OH)_2$ is precipitated with alkali hydroxide solutions. This precipitate dissolves in acids by giving Sn(II) salt and dissolves with the formation of stannite in excess reagent.

$$Sn^{2+} + 2OH^- \longrightarrow Sn(OH)_2$$

$$Sn(OH)_2 + 2H^+ \longrightarrow Sn^{2+} + 2H_2O$$

$$Sn(OH)_2 + 2OH^- \longrightarrow [Sn(OH)_4]^{2-}$$

3. 1-2 drops of Sn (II) solution diluted to approximately 0.5 mL is acidified with 2-3 drops of HCl. 4 drops of 0.1 M FeCl3 and 6 drops of 5% potassium tartrate solutions are added. Then, 2-3 drops of dimethylglyoxime and 6 drops of 4.0 M NH_4OH are added to the solution. The solution's color turns red.

Remark 1: If there is a possibility of the presence of tin with +4 oxidation number, the test is started after Sn(IV) is reduced with iron dust.

Remark 2: The main role of tartrate is to prevent the precipitation of Fe^{3+} in the form of iron (III) hydroxide, and to form a complex.

Remark 3: Dimethylglyoxime solution is 1% (v / v) Sn(II) solution in alcohol.

Remark 4: Since Ni^{2+}, Co^{2+} and UO_2^{2+} give the same color, and Cu^{2+}, Cr^{3+}, Mn^{2+}, Pb^{2+} give different colors, they negatively affect the determination procedure.

4. Fluorescence Test

Concentrated HCl and zinc are added into a porcelain capsule and then the tin-containing sample is added. The bottom of the test tube which is half-filled with cold water, is dipped

into this solution and then with the contact of reduced part of burning flame, a blue fluorescence is observed.

*Sn(IV) Ion

1. Tin (IV) halides, nitrates and sulfates hydrolyze as follows:

$$2SnCl_4 + 4H_2O \longrightarrow H_2[SnCl_6] + H_2[SnCl_2(OH)_4]$$

$$Sn(NO_3)_4 + (n+2)H_2O \longrightarrow SnO_2 . nH_2O \downarrow + 4HNO_3$$

$$Sn(SO_4)_2 + (n+2)H_2O \longrightarrow SnO_2 . nH_2O \downarrow + 2H_2SO_4$$

2. In an acidic medium, yellow colored SnS_2 precipitates are formed with H_2S. This precipitate dissolves in concentrated HCl and also in alkali sulfur and ammonium sulfide solutions by giving thiostannate anion.

$$H_2[SnCl_6] + 2H_2S \longrightarrow SnS_2 \downarrow + 6HCl$$

$$SnS_2 + (NH_4)_2S \longrightarrow (NH_4)_2SnS_3$$

If the thiostannate solution is acidified, SnS_2 will precipitate again.

$$(NH_4)_2SnS_3 + 2H^+ \longrightarrow SnS_2 \downarrow + H_2S + 2NH_4^+$$

3. The white colored $Sn(OH)_4$ tin (IV) hydroxide (stannic acid) produced with alkaline hydroxide solutions has amphoteric property. This solution dissolves in excess reagent and in acids.

$$[SnCl_6]^{2-} + 4OH^- \longrightarrow Sn(OH)_4 + 6Cl^-$$

$$Sn(OH)_4 + 2OH^- \longrightarrow [Sn(OH)_6]^{2-}$$

$$Sn(OH)_4 + 6HCl \longrightarrow H_2[SnCl_6] + 4H_2O$$

*As (III) Ion

1. Reaction with H_2S in acidic medium results in yellow colored As_2S_3 precipitates. If the medium is not strongly acidified, precipitates cannot be obtained, resulting in colloidal arsenic sulfur.

$$2H_3AsO_3 + 6HCl \longrightarrow 2AsCl_3 + 6H_2O$$

$$2AsCl_3 + 3H_2S \longrightarrow As_2S_3 \downarrow + 6HCl$$

It dissolves with alkali hydroxide, alkali carbonate, ammonium hydroxide and ammonium carbonate by giving oxathiolane salts.

$$As_2S_3 + 6NH_4OH \longrightarrow (NH_4)_3AsO_2S + (NH_4)_3AsOS_2 + 3H_2O$$

It dissolves by giving thioarsenite with ammonium sulphide and alkali sulphides.

$$As_2S_3 + 3(NH_4)_2S \longrightarrow 2(NH_4)_3AsS_3$$

The thioarsenite, which is formed by ammonium polysulfide, is oxidized into thioarsenate.

$$(NH_4)_3AsS_3 + (NH_4)_2S_2 \longrightarrow (NH_4)_3AsS_4 + (NH_4)_2S$$

As_2S_3 is not soluble in HCl and dilute H_2SO_4 but if it is boiled with concentrated HNO_3, it dissolves by oxidation.

$$3\,As_2S_3 + 10HNO_3 + 4H_2O \longrightarrow 6H_3AsO_4 + 10NO + 9S$$

If thio salts are acidified, As_2S_3 precipitates again.

$$2AsS_3^{3-} + 6H^+ \longrightarrow As_2S_3 \downarrow + 3H_2S$$

2. Yellow silver arsenide is precipitated with $AgNO_3$ solution.

$$[H_2AsO_3]^- + 3Ag^+ \longrightarrow Ag_3AsO_3 \downarrow + 2H^+$$

This precipitate is soluble in dilute HNO_3 and NH_4OH.

$$Ag_3AsO_3 + 6NH_4OH \longrightarrow 3[Ag(NH_3)_2]^+ + H_2AsO_3^- + 2OH^- + 4H_2O$$

3. Arsenic(III) forms a yellowish green precipitate with copper(II) in weakly basic medium.

$$NaH_2AsO_3 + Cu^{2+} + 2OH^- \longrightarrow Na[CuAsO_3] + 2H_2O$$

If this precipitate is filtered and then treated with NaOH solution, it dissolves by giving a blue colored solution. When the solution is heated, it gives reddish-brown Cu_2O precipitate.

$$2Na[CuAsO_3] + 2NaOH \longrightarrow NaH_2AsO_3 + Na_3AsO_4 + Cu_2O \downarrow$$

4. Arsenic (III) is oxidized to arsenic (V) while in a neutral or weakly basic medium while removing the color of the iodine solution.

$$[H_2AsO_3]^- + I_3^- + H_2O \longrightarrow [H_2AsO_4]^- + 3I^- + 2H^+$$

In order to neutralize the H^+ ion formed in the reaction, the HCO_3^- ion must be present in the medium.

*As(V) Ion

1. This ion gives a yellow precipitate of As_2S_5 with H_2S in an acidic medium. This precipitate dissolves in HNO_3 by giving arsenate, and in $(NH_4)_2S$ and $(NH_4)_2S_2$ by giving thioarsenate ion.

$$2AsO_4^{3-} + 5H_2S + 6H^+ \longrightarrow As_2S_5 \downarrow + 8H_2O$$

$$As_2S_5 + 10HNO_3 \longrightarrow 2H_3AsO_4 + 10NO_2 + 5S + 2H_2O$$

$$3(NH_4)_2S + As_2S_5 \longrightarrow 2(NH_4)_3AsS_4$$

2. Marsh Experiment: Add zinc grains and a few mL of diluted H_2SO_4 (or a small amount of metallic aluminum and a few mL of dilute NaOH solution) to the sample. The tube is closed with a cork with a thin glass tube passing through as seen in the figure. Discharge the air by carefully heating the air inside (Caution: Explosive gas mixture). Continue heating and burn out the released gas. If the obtained flame is held in the correct porcelain capsule, arsenic mirror occurs. Elemental As is soluble in ammonia H_2O_2 or NaClO solutions. This avoids a misleading stain that can be formed from Zn. (If Al and dilute NaOH solutions are used, only As is collected on the capsule).

$$H_3AsO_3 + 3Zn + 6H^+ \longrightarrow H_3As \uparrow + 3Zn^{2+} + 3H_2O$$

$$2H_3As \longrightarrow 2As + 3H_2 \uparrow$$

$$2As + 5H_2O_2 \longrightarrow 2H_3AsO_4 + 2H_2O$$

3. In an acidic medium, iodide is oxidized to iodine.

$$H_3AsO_4 + 3I^- + 2H^+ \longrightarrow H_3AsO_3 + I_3^- + H_2O$$

4. A brown precipitate is formed upon reaction with $AgNO_3$ solution.

$$3Ag^+ + AsO_4^{3-} \longrightarrow Ag_3AsO_4 \downarrow$$

5. It forms an ammonium molybdate arsenate precipitate with ammonium molybdate. (Ps. anion analysis)

Mo(VI) Ion

1. In an acidic environment, dark brown MoS_3 precipitates under the effect of H_2S. This precipitate dissolves in ammonium sulfide by giving a red colored thiomolybdate.

$$MoO_4^{2-} + 3H_2S + 2H^+ \longrightarrow MoS_3 \downarrow + 4H_2O$$

$$MoS_3 + (NH_4)_2S \longrightarrow 2(NH_4)_2MoS_4$$

2. When an acidified $SnCl_2$ solution is added to the molybdate solution, the Mo (VI) ion is reduced to Mo (V). The addition of the Mo (V) ion to the ammonium thiocyanate solution gives a dark red complex ion.

$$2MoO_4^{2-} + Sn^{2+} + 12H^+ + 10SCN^- \longrightarrow [MoO(SCN)_5]^{2-} + Sn^{4+} + 6H_2O$$

The Fe^{3+} ion which gives the complex with the same color as the thiocyanate anion is bound to $[Fe(PO_4)_2]^{3-}$ complex ion by the addition of H_3PO_4. Other reactions of MoO_4^{2-} anion: (See anion analysis)

4.5. HCl Group (Group I)

The $Ag^+, Hg_2^{2+}, Pb^{2+}, Tl^+$ ions present in this group give chlorides, and WO_4^{2-} ions in the form of H_2WO_4 in solution with 1 mL HCl. The use of concentrated HCl is disadvantageous because it will dissolve certain chlorides in complex formation. In addition, $PbCl_2$ is dissolved in hot water and, also a small amount dissolves in cold water, PbS precipitates too in the H_2S group.

Hg_2^{2+} Ion

1. The white Hg_2Cl_2 precipitate which is formed with dilute HCl or soluble chlorides, is insoluble in excess reagent, but soluble in HNO_3.

$$Hg_2^{2+} + 2Cl^- \longrightarrow Hg_2Cl_2$$

$$3Hg_2Cl_2 + 8HNO_3 \longrightarrow 3HgCl_2 + 3Hg(NO_3)_2 + 2NO\uparrow + 4H_2O$$

If NH_4OH is added to the Hg_2Cl_2 precipitate, the white colored aminomercury (I) chloride precipitates first. Instead of two hydrogens, this complex is assumed to be like NH_4CI with two mercury (I) ions and is stable. This complex is decomposed into aminomercury(II) chloride and metallic mercury by turning black.

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow NH_2Hg_2Cl\downarrow + NH_4^+ + 2H_2O + Cl^-$$

2. Mercury(II) oxide precipitates with alkali hydroxide solutions. Here, the precipitate becomes black as the finely dispersed metallic mercury covers the yellow colored HgO.

$$Hg_2^{2+} + 2OH^- \longrightarrow Hg\downarrow + HgO\downarrow + H_2O$$

3. The KI solution gives green-colored mercury (I) iodide precipitates. Mercury (I) iodide decomposes slightly by giving mercury (II) iodide and metallic mercury.

$$Hg_2^{2+} + 2I^- \longrightarrow Hg_2I_2$$

$$Hg_2I_2 \longrightarrow HgI_2 + Hg$$

4. With potassium chromate solution, it gives a red precipitate that is insoluble in dilute HNO_3 and bases, but hardly dissolved in concentrated HNO_3.

$$Hg_2^{2+} + CrO_4^{2-} \longrightarrow Hg_2CrO_4$$

5. Reduction of Hg_2^{2+} ion to metallic mercury;

    a. If 2-3 drops of $SnCl_2$ solution are dropped on the Hg_2Cl_2 precipitate, the precipitate becomes black due to the formation of metallic mercury.

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$$

    b. If a drop of $Hg_2(NO_3)_2$ solution is dropped on the copper plate, the metallic mercury is removed.

$$Hg_2^{2+} + Cu \longrightarrow Cu^{2+} + 2Hg \downarrow$$

6. In an acidic medium, it gives a precipitate of HgS consisting H_2S and Hg.

$$Hg_2^{2+} + H_2S \longrightarrow HgS \downarrow + Hg \downarrow + 2H^+$$

*Ag$^+$ Ion

1. White silver chloride formed with dilute HCl or soluble chloride is soluble in dilute NH$_4$OH.

$$Ag^+ + Cl^- \longrightarrow AgCl \downarrow$$

$$AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Cl + 2H_2O$$

The silver chloride precipitate is soluble in cyanide, thiosulfate and concentrated HCl by complex formation.

$$AgCl + 2CN^- \longrightarrow [Ag(CN)_2]^- + Cl^-$$

$$AgCl + 2S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-} + Cl^-$$

$$AgCl + 2HCl \longrightarrow H_2[AgCl_3]$$

2. This ion is precipitated in bromide and iodide solutions as yellowish silver bromide and light yellow silver iodide, respectively.

$$Ag^+ + Br^- \longrightarrow AgBr \downarrow$$

$$Ag^+ + I^- \longrightarrow AgI \downarrow$$

3. The red colored Ag_2CrO_4 precipitate is formed from K_2CrO_4 solution at pH 7. This precipitate is soluble in strong acids and NH_4OH. If the precipitation medium is basic, Ag_2O is precipitated instead of Ag_2CrO_4.

$$2Ag^+ + CrO_4^{2-} \longrightarrow Ag_2CrO_4$$

4. The intermediate product with alkali hydroxide solutions AgOH, is immediately converted to brown Ag_2O.

$$2Ag^+ + 2OH^- \longrightarrow 2AgOH\downarrow$$

$$2AgOH \longrightarrow Ag_2O\downarrow + H_2O$$

Ag_2O precipitate is dissolved in NH_4OH.

$$Ag_2O + 4NH_4OH \longrightarrow 2[Ag(NH_3)_2]^+ + 2OH^- + 3H_2O$$

5. With chromic acid, sodium hydroxide or organic solvents, a few drops of silver solution is put into the oil-stripped test tube. If necessary, dilute the solution with 5 - 10 drops of water. Firstly, 8-10 drops of 2N NH_4OH and a few drops of diluted formaldehyde solution are added, and then heated in a water bath. After that, the inner surface of the tube is observed to be coated with silver mirror.

$$Ag^+ + 2NH_4OH \longrightarrow [Ag(NH_3)_2]^+ + 2H_2O$$

$$[Ag(NH_3)_2]^+ + HCOH + H_2O \longrightarrow Ag\downarrow + HCOONH_4 + H^+ + NH_4^+$$
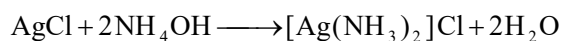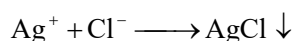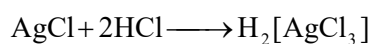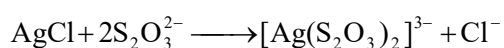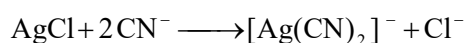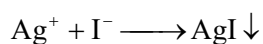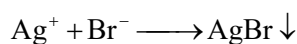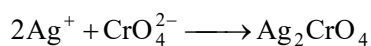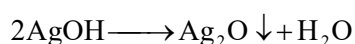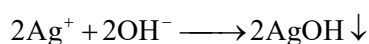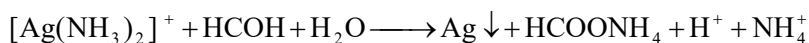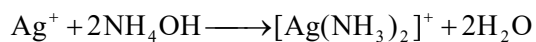
5. ORE ANALYSIS

Alloys and ores come from one or more elements or chemical compounds and their properties change depending on the composition and structure.

The ore samples to be analyzed are divided into 3 sections. These are:

1) Preliminary tests and analyzes to be made for control,

2) Systematic identification of cations,

3) Systematic identification of anions

Within the preliminary experiments; The color of the ore content, the shape and size of the particles that it contains and the results of the applied flame tests are important. In order to increase the reliability of the analysis result, results obtained in preliminary experiments must be evaluated with observations and results of systematic analysis. In addition, the sample of the ore should be evaluated for homogeneity and small particles. If the sample is not homogeneous, it should be finely pulverized in an agate mortar or porcelain, and then be homogenized by passing through a fine sieve.

Before systematic analysis are made, the sample must be dissolved into solution. The exact dissolution of the sample is based on solubilization and since the composition of the sample is unknown, a trial and error method is applied to find the appropriate solvent for solubilization. The methods used for solubilization are water, acids, bases and melting methods, respectively.

The solvents used in aqueous medium are classified according to the order of their use:

1) Water
2) Diluted HCl
3) Concentrated HCl
4) Diluted HNO_3
5) Concentrated HNO_3
6) Diluted H_2SO_4
7) Concentrated H_2SO_4
8) Acid mixtures (aqua rgia)
9) Basic dissolution
Heating may also be applied to speed up the dissolution process. Once the dissolution is complete, systematic analysis procedures are performed for anion and cation analyzes.

6. APPENDICES

Chart APPENDIX-1. Standard Reduction Potentials (25 ° C) *
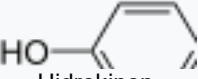
* s: solid; l: liquid; g: gas; aq: refers to the aqueous solution.

Half Reaction			$E°$ (V)
Oxidation	$\rightleftharpoons$	**Reduction**	
$Li^+ + e^-$		$Li(s)$	−3.0401
$Cs^+ + e^-$		$Cs(s)$	−3.026
$Rb^+ + e^-$		$Rb(s)$	−2.98
$K^+ + e^-$		$K(s)$	−2.931
$Ba^{2+} + 2e^-$		$Ba(s)$	−2.912
$Sr^{2+} + 2e^-$		$Sr(s)$	−2.899
$Ca^{2+} + 2e^-$		$Ca(s)$	−2.868
$Na^+ + e^-$		$Na(s)$	−2.71
$Mg^{2+} + 2e^-$		$Mg(s)$	−2.372
$Ce^{3+} + 3e^-$		Ce	−2.336
$Al(OH)_3(s) + 3e^-$		$Al(s) + 3OH^-$	−2.31
$AlF_6^{3-} + 3e^-$		$Al + 6\ F^-$	−2.069
$H_2BO_3^- + H_2O + 3e^-$		$B + 4\ OH^-$	−1.79
$SiO_3^{2-} + H_2O + 4e^-$		$Si + 6\ OH^-$	−1.697
$Al^{3+} + 3e^-$		$Al(s)$	−1.662
$Ti^{2+} + 2e^-$		$Ti(s)$	−1.63
$ZrO_2(s) + 4H^+ + 4e^-$		$Zr(s) + 2H_2O$	−1.553
$Zr^{4+} + 4e^-$		$Zr(s)$	−1.45

$Ti^{3+} + 3e^-$	$Ti(s)$	−1.37
$TiO(s) + 2\underline{H}^+ + 2e^-$	$Ti(s) + \underline{H_2O}$	−1.31
$\underline{Ti_2O_3}(s) + 2\underline{H}^+ + 2e^-$	$2TiO(s) + \underline{H_2O}$	−1.23
$Zn(OH)_4{}^{2-} + 2e^-$	$Zn(s) + 4\underline{OH}^-$	−1.199
$\underline{Mn}^{2+} + 2e^-$	$Mn(s)$	−1.185
$\underline{Fe}(CN)_6{}^{4-} + 6\underline{H}^+ + 2\ e^-$	$Fe(s) + 6HCN(aq)$	−1.16
$\underline{Te}(s) + 2e^-$	Te^{2-}	−1.143
$\underline{V}^{2+} + 2e^-$	$V(s)$	−1.13
$\underline{Sn}(s) + 4\underline{H}^+ + 4e^-$	$SnH_4(g)$	−1.07
$\underline{SiO_2}(s) + 4\underline{H}^+ + 4e^-$	$Si(s) + 2\underline{H_2O}$	−0.91
$\underline{B(OH)_3}(aq) + 3\underline{H}^+ + 3e^-$	$B(s) + 3\underline{H_2O}$	−0.89
$Fe(OH)_2(s) + 2e^-$	$Fe(s) + 2\underline{OH}^-$	−0.89
$Fe_2O_3(s) + 3\underline{H_2O} + 2e^-$	$2Fe(OH)_2(s) + 2\underline{OH}^-$	−0.86
$TiO^{2+} + 2\underline{H}^+ + 4e^-$	$Ti(s) + \underline{H_2O}$	−0.86
$2\underline{H_2O} + 2e^-$	$H_2(g) + 2\underline{OH}^-$	−0.8277
$\underline{Bi}(s) + 3\underline{H}^+ + 3e^-$	$\underline{BiH_3}$	−0.8
$\underline{Zn}^{2+} + 2e^-$	$Zn(s)$	−0.7618
$\underline{Cr}^{3+} + 3e^-$	$Cr(s)$	−0.74
$\underline{Ag_2S}(s) + 2e^-$	$2Ag(s) + \underline{S}^{2-}(aq)$	−0.69
$[Au(CN)_2]^- + e^-$	$\underline{Au}(s) + 2CN^-$	−0.60
$PbO(s) + \underline{H_2O} + 2e^-$	$Pb(s) + 2\underline{OH}^-$	−0.58
$2TiO_2(s) + 2\underline{H}^+ + 2e^-$	$Ti_2O_3(s) + \underline{H_2O}$	−0.56
$U^{4+} + e^-$	U^{3+}	−0.52

$S_{(s)} + 2e^-$		S^{2-}	-0.48
$\underline{Fe}^{2+} + 2e^-$		$Fe(s)$	−0.44
$2\underline{CO_2}(g) + 2\underline{H}^+ + 2e^-$		$\underline{HOOCCOOH}(aq)$ $(H_2C_2O_4)(aq)$	−0.43
$Cr^{3+} + e^-$		Cr^{2+}	−0.42
$\underline{Cd}^{2+} + 2e^-$		$Cd(s)$	−0.40
$\underline{Cu_2O}(s) + \underline{H_2O} + 2e^-$		$2Cu(s) + 2\underline{OH}^-$	−0.360
$\underline{PbSO_4}(s) + 2e^-$		$\underline{Pb}(s) + SO_4^{2-}$	−0.3588
$\underline{Tl}^+ + e^-$		$Tl(s)$	−0.34
$\underline{Co}^{2+} + 2e^-$		$Co(s)$	−0.28
$\underline{H_3PO_4}(aq) + 2\underline{H}^+ + 2e^-$		$H_3PO_3(aq) + \underline{H_2O}$	−0.276
$V^{3+} + e^-$		V^{2+}	−0.26
$\underline{Ni}^{2+} + 2e^-$		$Ni(s)$	−0.25
$\underline{As}(s) + 3\underline{H}^+ + 3e^-$		$\underline{AsH_3}(g)$	−0.23
$\underline{AgI}(s) + e^-$		$Ag(s) + I^-$	−0.1522
$Sn^{2+} + 2e^-$		$Sn(s)$	−0.13
$O_2(g) + H^+ + e^-$		$HO_2\bullet(aq)$	−0.13
$Pb^{2+} + 2e^-$		$Pb(s)$	−0.126
$CO_2(g) + 2H^+ + 2e^-$		$HCOOH(aq)$	−0.11
$Se(s) + 2H^+ + 2e^-$		$H_2Se(g)$	−0.11
$CO_2(g) + 2H^+ + 2e^-$		$CO(g) + H_2O$	−0.11
$SnO(s) + 2H^+ + 2e^-$		$Sn(s) + H_2O$	−0.10
$SnO_2(s) + 4H^+ + 4e^-$		$SnO(s) + 2H_2O$	−0.09
$Fe^{3+} + 3e^-$		$Fe(s)$	−0.04

$HCOOH(aq) + 2H^+ + 2e^-$	$HCHO(aq) + H_2O$	−0.03
$2H^+ + 2e^-$	$H_2(g)$	0.0000
$AgBr(s) + e^-$	$Ag(s) + Br^-$	+0.0713
$S_4O_6^{2-} + 2e^-$	$2S_2O_3^{2-}$	+0.08
$Fe_3O_4(s) + 8H^+ + 8e^-$	$3Fe(s) + 4H_2O$	+0.085
$N_2(g) + 2H_2O + 6H^+ + 6e^-$	$2NH_4OH(aq)$	+0.092
$HgO(s) + H_2O + 2e^-$	$Hg(l) + 2OH^-$	+0.0977
$Cu(NH_3)_4^{2+} + e^-$	$Cu(NH_3)_2^+ + 2NH_3$	+0.10
$N_2H_4(aq) + 4H_2O + 2e^-$	$2NH_4^+ + 4OH^-$	+0.11
$H_2MoO_4(aq) + 6H^+ + 6e^-$	$Mo(s) + 4H_2O$	+0.11
$C(s) + 4H^+ + 4e^-$	$CH_4(g)$	+0.13
$HCHO(aq) + 2H^+ + 2e^-$	$CH_3OH(aq)$	+0.13
$S(s) + 2H^+ + 2e^-$	$H_2S(g)$	+0.14
$Sn^{4+} + 2e^-$	Sn^{2+}	+0.15
$Cu^{2+} + e^-$	Cu^+	+0.159
$HSO_4^- + 3H^+ + 2e^-$	$SO_2(aq) + 2H_2O$	+0.16
$UO_2^{2+} + e^-$	UO_2^+	+0.163
$SO_4^{2-} + 4H^+ + 2e^-$	$SO_2(aq) + 2H_2O$	+0.17
$TiO^{2+} + 2H^+ + e^-$	$Ti^{3+} + H_2O$	+0.19
$SbO^+ + 2H^+ + 3e^-$	$Sb(s) + H_2O$	+0.20
$AgCl(s) + e^-$	$Ag(s) + Cl^-$	+0.2223
$H_3AsO_3(aq) + 3H^+ + 3e^-$	$As(s) + 3H_2O$	+0.24
$Hg_2Cl_2(s) + 2e^-$	$2Hg(l) + 2Cl^-(aq)$	0.268

$UO_2^+ + 4H^+ + e^-$	$U^{4+} + 2H_2O$	+0.273
$Bi^{3+} + 3e^-$	$Bi(s)$	+0.308
$Cu^{2+} + 2e^-$	$Cu(s)$	+0.337
$VO^{2+} + 2H^+ + e^-$	$V^{3+} + H_2O$	+0.34
$[Fe(CN)_6]^{3-} + e^-$	$[Fe(CN)_6]^{4-}$	+0.36
$O_2(g) + 2H_2O + 4e^-$	$4OH^-(aq)$	+0.401
$H_2MoO_4 + 6H^+ + 3e^-$	$Mo^{3+} + 2H_2O$	+0.43
$CH_3OH(aq) + 2H^+ + 2e^-$	$CH_4(g) + H_2O$	+0.50
$SO_2(aq) + 4H^+ + 4e^-$	$S(s) + 2H_2O$	+0.50
$Cu^+ + e^-$	$Cu(s)$	+0.520
$CO(g) + 2H^+ + 2e^-$	$C(s) + H_2O$	+0.52
$I_3^- + 2e^-$	$3I^-$	+0.53
$I_2(s) + 2e^-$	$2I^-$	+0.54
$[AuI_4]^- + 3e^-$	$Au(s) + 4I^-$	+0.56
$H_3AsO_4(aq) + 2H^+ + 2e^-$	$H_3AsO_3(aq) + H_2O$	+0.56
$MnO_4^- + 2H_2O + 3e^-$	$MnO_2(s) + 4OH^-$	1.692
$S_2O_3^{2-} + 6H^+ + 4e^-$	$2S(s) + 3H_2O$	+0.60
$BrO_3^- + 3H_2O + 6e^-$	$Br^- + 6OH^-$	0.61
$+ 2H^+ + 2e^-$ Kinon	 Hidrokinon	+0.6992
$O_2(g) + 2H^+ + 2e^-$	$H_2O_2(aq)$	+0.70
$Tl^{3+} + 3e^-$	$Tl(s)$	+0.72
$PtCl_6^{2-} + 2e^-$	$PtCl_4^{2-} + 2Cl^-$	+0.726

$H_2SeO_3(aq) + 4H^+ + 4e^-$	$Se(s) + 3H_2O$	+0.74
$PtCl_4^{2-} + 2e^-$	$Pt(s) + 4Cl^-$	+0.758
$Fe^{3+} + e^-$	Fe^{2+}	+0.77
$Ag^+ + e^-$	$Ag(s)$	+0.7996
$Hg_2^{2+} + 2e^-$	$2Hg(l)$	+0.80
$NO_3^-(aq) + 2H^+ + e^-$	$NO_2(g) + H_2O$	+0.80
$2FeO_4^{2-} + 5H_2O + 6e^-$	$Fe_2O_3(s) + 10\ OH^-$	+0.81
$Hg^{2+} + 2e^-$	$Hg(l)$	+0.85
$2Hg^{2+} + 2e^-$	Hg_2^{2+}	+0.91
$[AuCl_4]^- + 3e^-$	$Au(s) + 4Cl^-$	+0.93
$MnO_2(s) + 4H^+ + e^-$	$Mn^{3+} + 2H_2O$	+0.95
$NO_3^-(aq) + 4H^+ + 3e^-$	$NO(g) + 2H_2O(l)$	+0.958
$NO_2^- + 2\ H^+ + e^-$	$NO_{(g)} + H_2O$	+1.00
$[VO_2]^+(aq) + 2H^+ + e^-$	$[VO]^{2+}(aq) + H_2O$	+1.00
$Br_2(l) + 2e^-$	$2Br^-$	+1.066
$Br_2(aq) + 2e^-$	$2Br^-$	+1.0873
$IO_3^- + 6\ H^+ + 6\ e^-$	$I^- + 3\ H_2O$	+1.08
$IO_3^- + 5H^+ + 4e^-$	$HIO(aq) + 2H_2O$	+1.13
$HSeO_4^- + 3H^+ + 2e^-$	$H_2SeO_3(aq) + H_2O$	+1.15
$ClO_3^- + 2H^+ + e^-$	$ClO_2(g) + H_2O$	+1.18
$Pt^{2+} + 2e^-$	$Pt(s)$	+1.188
$ClO_2(g) + H^+ + e^-$	$HClO_2(aq)$	+1.19
$2IO_3^- + 12H^+ + 10e^-$	$I_2(s) + 6H_2O$	+1.20

$ClO_4^- + 2H^+ + 2e^-$		$ClO_3^- + H_2O$	+1.20
$O_2(g) + 4H^+ + 4e^-$		$2H_2O$	+1.229
$MnO_2(s) + 4H^+ + 2e^-$		$Mn^{2+} + 2H_2O$	+1.23
$Tl^{3+} + 2e^-$		Tl^+	+1.25
$Cr_2O_7^{2-} + 14H^+ + 6e^-$		$2Cr^{3+} + 7H_2O$	+1.33
$ClO_4^- + 8H^+ + 8e-$		$Cl^- + 4H_2O$	+1.34
$Cl_2(g) + 2e^-$		$2Cl^-$	+1.36
$2NH_3OH^+ + H^+ + 2e^-$		$N_2H_5^+ + 2H_2O$	+1.42
$2HIO(aq) + 2H^+ + 2e^-$		$I_2(s) + 2H_2O$	+1.44
$BrO_3^- + 6H^+ + 6e^-$		$Br^- + 3H_2O$	+1.44
$ClO_3^- + 6H^+ + 6e^-$		$Cl^- + 3H_2O$	+ 1.45
$BrO_3^- + 5H^+ + 4e^-$		$HBrO(aq) + 2H_2O$	+1.45
$\alpha\text{-}PbO_2(s) + 4H^+ + 2e^-$		$Pb^{2+} + 2H_2O$	+1.468
$2BrO_3^- + 12H^+ + 10e^-$		$Br_2(l) + 6H_2O$	+1.48
$2ClO_3^- + 12H^+ + 10e^-$		$Cl_2(g) + 6H_2O$	+1.49
$HClO(aq) + H^+ + 2e^-$		$Cl^-(aq) + H_2O$	+1.49
$MnO_4^- + 8H^+ + 5e^-$		$Mn^{2+} + 4H_2O$	+1.51
$HO_2^{\cdot} + H^+ + e^-$		$H_2O_2(aq)$	+1.51
$Au^{3+} + 3e^-$		$Au(s)$	+1.52
$Ce^{4+} + e^-$		Ce^{3+}	+1.61
$2HClO(aq) + 2H^+ + 2e^-$		$Cl_2(g) + 2H_2O$	+1.63
$HClO_2(aq) + 2H^+ + 2e^-$		$HClO(aq) + H_2O$	+1.67
$Pb^{4+} + 2e^-$		Pb^{2+}	+1.69

$MnO_4^- + 4H^+ + 3e^-$	$MnO_2(s) + 2H_2O$	+1.70
$AgO(s) + 2H^+ + e^-$	$Ag^+ + H_2O$	+1.77
$H_2O_2(aq) + 2H^+ + 2e^-$	$2H_2O$	+1.78
$Co^{3+} + e^-$	Co^{2+}	+1.82
$Au^+ + e^-$	$Au(s)$	+1.83
$Ag^{2+} + e^-$	Ag^+	+1.98
$S_2O_8^{2-} + 2e^-$	$2SO_4^{2-}$	+2.010
$O_3(g) + 2H^+ + 2e^-$	$O_2(g) + H_2O$	+2.075
$FeO_4^{2-} + 3e^- + 8H^+$	$Fe^{3+} + 4H_2O$	+2.20
$F_2(g) + 2e^-$	$2F^-$	+2.87

Chart APPENDIX-2. Solubility Products of Slightly Soluble Salts in Water *

Formula	K_{sp}	Formula	K_{sp}
$AlPO_4$	9.84×10^{-21}	$PbBr_2$	6.60×10^{-6}
$Ba(BrO_3)_2$	2.43×10^{-4}	$PbCO_3$	7.40×10^{-14}
$BaCO_3$	2.58×10^{-9}	$PbCl_2$	1.70×10^{-5}
$BaCrO_4$	1.17×10^{-10}	PbF_2	3.3×10^{-8}
BaF_2	1.84×10^{-7}	$Pb(OH)_2$	1.43×10^{-20}
$Ba(IO_3)_2$	4.01×10^{-9}	$Pb(IO_3)_2$	3.69×10^{-13}
$Ba(NO_3)_2$	4.64×10^{-3}	PbI_2	9.8×10^{-9}
$BaSO_4$	1.08×10^{-10}	$PbSeO_4$	1.37×10^{-7}
$BaSO_3$	5.0×10^{-10}	$PbSO_4$	2.53×10^{-8}
$Be(OH)_2$	6.92×10^{-22}	PbS	8.0×10^{-28}
$BiAsO_4$	4.43×10^{-10}	Li_2CO_3	8.15×10^{-4}
BiI_3	7.71×10^{-19}	LiF	1.84×10^{-3}
$CdCO_3$	1.0×10^{-12}	Li_3PO_4	2.37×10^{-11}
CdF_2	6.44×10^{-3}	$MgCO_3$	6.82×10^{-6}
$Cd(OH)_2$	7.2×10^{-15}	MgF_2	5.16×10^{-11}
$Cd(IO_3)_2$	2.5×10^{-8}	$Mg(OH)_2$	5.61×10^{-12}
$Cd_3(PO_4)_2$	2.53×10^{-33}	$Mg_3(PO_4)_2$	1.04×10^{-24}
CdS	8.0×10^{-27}	$MnCO_3$	2.24×10^{-11}
$CaCO_3$	3.36×10^{-9}	$Mn(IO_3)_2$	4.37×10^{-7}
CaF_2	3.45×10^{-11}	Hg_2Br_2	6.40×10^{-23}
$Ca(OH)_2$	5.02×10^{-6}	Hg_2CO_3	3.6×10^{-17}
$Ca(IO_3)_2$	6.47×10^{-6}	Hg_2Cl_2	1.43×10^{-18}
$Ca_3(PO_4)_2$	2.07×10^{-33}	Hg_2F_2	3.10×10^{-6}
$CaSO_4$	4.93×10^{-5}	Hg_2I_2	5.2×10^{-29}
$CsClO_4$	3.95×10^{-3}	$Hg_2C_2O_4$	1.75×10^{-13}

Formula	K_{sp}	Formula	K_{sp}
$CsIO_4$	5.16×10^{-6}	Hg_2SO_4	6.5×10^{-7}
$Co_3(AsO_4)_2$	6.80×10^{-29}	$Hg_2(SCN)_2$	3.2×10^{-20}
$Co(OH)_2$	5.92×10^{-15}	$HgBr_2$	6.2×10^{-20}
$Co_3(PO_4)_2$	2.05×10^{-35}	HgI_2	2.9×10^{-29}
$CuBr$	6.27×10^{-9}	HgS	4×10^{-53}
$CuCl$	1.72×10^{-7}	HgS	1.6×10^{-52}
$CuCN$	3.47×10^{-20}	$Nd_2(CO_3)_3$	1.08×10^{-33}
CuI	1.27×10^{-12}	$NiCO_3$	1.42×10^{-7}
$CuSCN$	1.77×10^{-13}	$Ni(OH)_2$	5.48×10^{-16}
$Cu_3(AsO_4)_2$	7.95×10^{-36}	$Ni(IO_3)_2$	4.71×10^{-5}
CuC_2O_4	4.43×10^{-10}	$Ni_3(PO_4)_2$	4.74×10^{-32}
$Cu_3(PO_4)_2$	1.40×10^{-37}	$Pd(SCN)_2$	4.39×10^{-23}
CuS	6.3×10^{-36}	K_2PtCl_6	7.48×10^{-6}
$Eu(OH)_3$	9.38×10^{-27}	$KClO_4$	1.05×10^{-2}
$Ga(OH)_3$	7.28×10^{-36}	KIO_4	3.71×10^{-4}
$FeCO_3$	3.13×10^{-11}	$Pr(OH)_3$	3.39×10^{-24}
FeF_2	2.36×10^{-6}	$RbClO_4$	3.00×10^{-3}
$Fe(OH)_2$	4.87×10^{-17}	ScF_3	5.81×10^{-24}
$Fe(OH)_3$	2.79×10^{-39}	$Sc(OH)_3$	2.22×10^{-31}
FeS	6.3×10^{-18}	$AgCH_3CO_2$	1.94×10^{-3}
$La(IO_3)_3$	7.50×10^{-12}	Ag_3AsO_4	1.03×10^{-22}
$AgBrO_3$	5.38×10^{-5}	$TlBr$	3.71×10^{-6}
$AgBr$	5.35×10^{-13}	$TlCl$	1.86×10^{-4}
Ag_2CO_3	8.46×10^{-12}	Tl_2CrO_4	8.67×10^{-13}
$AgCl$	1.77×10^{-10}	$TlIO_3$	3.12×10^{-6}
Ag_2CrO_4	1.12×10^{-12}	TlI	5.54×10^{-8}

Formula	K_{sp}	Formula	K_{sp}
AgCN	5.97×10^{-17}	TlSCN	1.57×10^{-4}
AgIO$_3$	3.17×10^{-8}	Tl(OH)$_3$	1.68×10^{-44}
AgI	8.52×10^{-17}	Sn(OH)$_2$	5.45×10^{-27}
Ag$_2$C$_2$O$_4$	5.40×10^{-12}	SnS	1.0×10^{-25}
Ag$_3$PO$_4$	8.89×10^{-17}	Y$_2$(CO$_3$)$_3$	1.03×10^{-31}
Ag$_2$SO$_4$	1.20×10^{-5}	YF$_3$	8.62×10^{-21}
Ag$_2$S	6.3×10^{-50}	Y(OH)$_3$	1.00×10^{-22}
Ag$_2$SO$_3$	1.50×10^{-14}	Y(IO$_3$)$_3$	1.12×10^{-10}
AgSCN	1.03×10^{-12}	Zn$_3$(AsO$_4$)$_2$	2.8×10^{-28}
Sr$_3$(AsO$_4$)$_2$	4.29×10^{-19}	ZnCO$_3$	1.46×10^{-10}
SrCO$_3$	5.60×10^{-10}	ZnF$_2$	3.04×10^{-2}
SrF$_2$	4.33×10^{-9}	Zn(OH)$_2$	3×10^{-17}
Sr(IO$_3$)$_2$	1.14×10^{-7}	ZnSe	3.6×10^{-26}
SrSO$_4$	3.44×10^{-7}	ZnS	1.6×10^{-24}
TlBrO$_3$	1.10×10^{-4}	ZnS	2.5×10^{-22}

Chart APPENDIX-3. Formation Constants of Some Complex Ions (25 ^{o}C) *

Complex ion	K_f	Complex ion	K_f
$[Ag(CN)_2]^-$	5.6×10^{18}	$[Cu(CN)_2]^-$	1.0×10^{16}
$[Ag(EDTA)]^{3-}$	2.1×10^7	$[Cu(CN)_4]^{3-}$	2.0×10^{30}
$[Ag(en)_2]^+$	5.0×10^7	$[Cu(SCN)_2]$	5.6×10^3
$[Ag(NH_3)_2]^+$	1.6×10^7	$[Cu(EDTA)]^{2-}$	5×10^{18}
$[Ag(SCN)_4]^{3-}$	1.2×10^{10}	$[Cu(en)_2]^{2+}$	1×10^{20}
$[Ag(S_2O_3)_2]^{3-}$	1.7×10^{13}	$[Cu(CN)_4]^{2-}$	1×10^{25}
$[AgCl_2]^{-1}$	1.8×10^5	$[Cu(NH_3)_4]^{2+}$	1.1×10^{13}
$[AgBr_2]^{-1}$	1.0×10^{11}	$[Cu(ox)_2]^{2-}$	3×10^8
$[AgI_2]^{-1}$	1.0×10^{11}	$[Co(NH_3)_6]^{2+}$	1.3×10^5
$[Al(EDTA)]^-$	1.3×10^{16}	$[Co(NH_3)_6]^{3+}$	4.5×10^{33}
$[Al(OH)_4]^-$	1.1×10^{33}	$[Co(en)_3]^{2+}$	8.7×10^{13}
$[Al(ox)_3]^{3-}$	2×10^{16}	$[Co(en)_3]^{3+}$	4.9×10^{48}
$[AlF_6]^{3-}$	2.5×10^4	$[Co(ox)_3]^{3-}$	1×10^{20}
$[AlF_4]^{-1}$	2.0×10^8	$[Co(ox)_3]^{4-}$	5×10^9
$[Cd(NH_3)_4]^{2+}$	1.3×10^7	$[Co(SCN)_4]^{2-}$	1.0×10^3
$[Cd(en)_3]^{2+}$	1.2×10^{12}	$[Co(EDTA)]^{2-}$	2.0×10^{16}
$[Cd(CN)_4]^{2-}$	6.0×10^{18}	$[Co(EDTA)]^-$	1×10^{36}
$[Cd(SCN)_4]^{2-}$	1.0×10^3	$[Cr(EDTA)]^-$	1×10^{23}
$[CuCl_3]^{2-}$	5×10^5	$[Cr(OH)_4]^-$	8×10^{29}
$[CuCl_2]^{-1}$	3.0×10^5	$[Fe(CN)_6]^{4-}$	1×10^{37}
$[CuBr_2]^{-1}$	8.0×10^5	$[Fe(CN)_6]^{3-}$	1×10^{42}
$[CuI_2]^{-1}$	8.0×10^8	$[Fe(SCN)_3]$	2.0×10^6
$[Fe(SCN)]^{2+}$	8.9×10^2	$[PbCl_3]^-$	2.4×10^1
$[Fe(EDTA)]^{2-}$	2.1×10^{14}	$[Ni(NH_3)_6]^{2+}$	5.5×10^8
$[Fe(EDTA)]^-$	1.7×10^{24}	$[Ni(ox)_3]^{4-}$	3×10^8
$[Fe(en)_3]^{2+}$	5.0×10^9	$[PbCl_4]^{2-}$	2.5×10^{15}
$[Fe(ox)_3]^{4-}$	1.7×10^5	$[PbI_4]^{2-}$	3.0×10^4

Complex Ion	K_f	Complex Ion	K_f
$[Fe(ox)_3]^{3-}$	2×10^{20}	$[Pb(OH)_3]^-$	3.8×10^{14}
$[Hg(CN)_4]^{2-}$	3×10^{41}	$[Pb(EDTA)]^{2-}$	2×10^{18}
$[Hg(SCN)_4]^{2-}$	5.0×10^{21}	$[Pb(ox)_2]^{2-}$	3.5×10^{6}
$[Hg(EDTA)]^{2-}$	6.3×10^{21}	$[Pb(S_2O_3)_3]^{4-}$	2.2×10^{6}
$[Hg(en)_2]^{2+}$	2×10^{23}	$[PtCl_4]^{2-}$	1×10^{16}
$[HgCl_4]^{2-}$	1.2×10^{15}	$[Pt(NH_3)_6]^{2+}$	2×10^{35}
$[HgI_4]^{2-}$	6.8×10^{29}	$[Zn(CN)_4]^{2-}$	1×10^{18}
$[HgBr_4]^{2-}$	3.0×10^{4}	$[Zn(EDTA)]^{2-}$	3×10^{16}
$[Hg(ox)_2]^{2-}$	9.5×10^{6}	$[Zn(en)_3]^{2+}$	1.3×10^{14}
$[Ni(CN)_4]^{2-}$	2×10^{31}	$[Zn(NH_3)_4]^{2+}$	4.1×10^{8}
$[Ni(EDTA)]^{2-}$	3.6×10^{18}	$[Zn(OH)_4]^{2-}$	4.6×10^{17}
$[Ni(en)_3]^{2+}$	2.1×10^{18}	$[Zn(ox)_3]^{4-}$	1.4×10^{8}

* Values measured in media with different ionic strengths are not separately specified.

Table APPENDIX 4 Ionization Constants of Some Acids (25 0C)*,‡,**

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Acetic Acid	CH_3CO_2H	1.75×10^{-5}		
Arsenate	H_3AsO_4	5.5×10^{-3}	1.7×10^{-7}	5.1×10^{-12}
Benzoic Acid	$C_6H_5CO_2H$	6.25×10^{-5}		
Boric Acid	H_3BO_3	$5.4 \times 10^{-10}*$	$>1 \times 10^{-14}*$	
Bromoacetic Acid	CH_2BrCO_2H	1.3×10^{-3}		
Carbonic Acid	H_2CO_3	4.5×10^{-7}	4.7×10^{-11}	
Chloroacetic Acid	CH_2ClCO_2H	1.3×10^{-3}		
Chloric Acid	$HClO_2$	1.1×10^{-2}		
Chromic Acid	H_2CrO_4	1.8×10^{-1}	3.2×10^{-7}	
Citric Acid	$C_6H_8O_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Dichloroacetic Acid	$CHCl_2CO_2H$	4.5×10^{-2}		
Fluoroacetic Acid	CH_2FCO_2H	2.6×10^{-3}		
Formic Acid	CH_2O_2	1.8×10^{-4}		
Hydrazoic Acid	HN_3	2.5×10^{-5}		
Hydrocyanic Acid	HCN	6.2×10^{-10}		
Hydrogen Cyanate	$HCNO$	3.5×10^{-4}		
Hydrofluoric Acid	HF	6.3×10^{-4}		
Hydrogen Sulfide	H_2S	8.9×10^{-8}	1×10^{-19}	
Hypobromic Acid	$HBrO$	2.8×10^{-9}		
Hypochloric Acid	$HClO$	4.0×10^{-8}		
Hypoiodic Acid	HIO	3.2×10^{-11}		
Iodic Acid	HIO_3	1.7×10^{-1}		
Iodoacetic Acid	CH_2ICO_2H	6.6×10^{-4}		
Nitrous Acid	HNO_2	5.6×10^{-4}		
Oxalic Acid	$C_2H_2O_4$	5.6×10^{-2}	1.5×10^{-4}	
Periodic Acid	HIO_4	2.3×10^{-2}		
Phenol	C_6H_5OH	1.0×10^{-10}		
Phosphoric Acid	H_3PO_4	6.9×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Phosphorous Acid	H_3PO_3	$5.0 \times 10^{-2}*$	$2.0 \times 10^{-7}*$	
Resorcinol	$C_6H_4(OH)_2$	4.8×10^{-10}	7.9×10^{-12}	
Selenic Acid	H_2SeO_4	Strong	2.0×10^{-2}	
Selenose Acid	H_2SeO_3	2.4×10^{-3}	4.8×10^{-9}	
Sulfuric Acid	H_2SO_4	Strong	1.0×10^{-2}	

Sulfurous Acid	H_2SO_3	1.4×10^{-2}	6.3×10^{-8}	
meso-Tartaric Acid	$C_4H_6O_6$	6.8×10^{-4}	1.2×10^{-5}	
Telluric Acid	H_2TeO_4	$2.1 \times 10^{-8\ddagger}$	$1.0 \times 10^{-11\ddagger}$	
Tellurous Acid	H_2TeO_3	5.4×10^{-7}	3.7×10^{-9}	
Trichloroacetic Acid	CCl_3CO_2H	2.2×10^{-1}		
Trifluoroacetic Acid	CF_3CO_2H	3.0×10^{-1}		

* Measured at 20 ° C ‡ Measured at 18 ° C
**https://chem.libretexts.org/Reference/Reference_Tables/Equilibrium_Constants *(CRC Handbook of Chemistry and Physics,* 84th Edition (2004)).

Table APPENDIX-5 Ionization Constants of Some Bases (25 0C) *

Name	Formula	K_b
Ammonia	NH_3	1.8×10^{-5}
Aniline	$C_6H_5NH_2$	7.4×10^{-10}
n-Butylamine	$C_4H_9NH_2$	4.0×10^{-4}
Sec-Butylamine	$(CH_3)_2CHCH_2NH_2$	3.6×10^{-4}
tert-Butylamine	$(CH_3)_3CNH_2$	4.8×10^{-4}
Dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}
Ethylamine	$C_2H_5NH_2$	4.5×10^{-4}
Hydrazine	N_2H_4	1.3×10^{-6}
Hydroxylamine	NH_2OH	8.7×10^{-9}
Methylamine	CH_3NH_2	4.6×10^{-4}
Propylamine	$C_3H_7NH_2$	3.5×10^{-4}
Pyridine	C_5H_5N	1.7×10^{-9}
Trimethylamine	$(CH_3)_3N$	6.3×10^{-5}

II- QUANTITATIVE ANALYSIS

Classical quantitative analysis methods are divided into two parts:

1. Gravimetry

2. Volumetry

The specific amount weighing from the material to be analyzed is dissolved by the appropriate method. The resulting solution is complete to a certain volume. Analysis is carried out by taking a certain amount of this solution.

1. GRAVIMETRY

Gravimetry is based on weighing only after converting the substance to be analyzed directly into a solid or a dissolving compound. In addition this, some compounds like that H_2O, CO_2 etc. can be determined by means of calculated loosing amounth of total weight.

The determined ion present in the solution is precipitated as a poorly soluble compound with a suitable reagent. The precipitate is digested, filtered, washed, dried and ignited, weighed.

1.1. Precipitation

During precipitation, the amount of residue in the solution should be less than the minimum amount that an analytical balance can weigh, less than 0,0001 g.

The type of precipitate should be suitable filtration and can be washed quickly. For this reason the precipitates in the crystal structure is wanted to be big granule. Because, if the precitate get big, it can be block the pore of filter paper or can pour the pore. In addition, unwanted ions are more adsorbed in the solution as the total surface increases.

After the precipitating substance is dried and ignited, the composition should be converted into a precise substance.

To complete the precipitation, the precipitating reagent should be added in an amount of   5-10% from the required amount. Participation of the excess of the reagent should be disadvantageous in some cases to cause the redeposition of the precipitate to be resolved, as well as to cause adsorption of the precipitate to contaminate the precipitate.

Excessive amounts of foreign ions in the solution should increase the solubility and not work in a concentrated environment.

Precipitates are crystallized or amorphous. To ensure that the crystals are coarse in the formation of crystallized precipitates and to prevent oversaturated solutions from forming:

1) The precipitation sufficiently diluted solution should be made by slow addition of the diluted reagent.

2) In order to avoid local over concentration, the addition of reagent should be done by mixing.

3) In order to slow down the crystal formation, precipitation must be done in the hot and complete by the addition of excess of reagent.

When amorphous precipitates are formed by coagulation of colloidal solutions, precipitation is occurred by heating the colloidal solutions or adding the coagulating electrolyte.

The amorphous $Fe(OH)_3$, $Al(OH)_3$ precipitates obtained from the dilute solutions are loose and bulky. They adsorb unwanted ions because of their surface area.

Amorphous precipitates should be small grains, unlike crystallized precipitates. Because the smaller particles are easier to collapse and adsorbs less foreign matter.

For this purpose, the solution should be concentrated in the amorphous precipitate formation, the process should be done in the hot.

After the sedimentation is complete, approximately 100 mL of water should be added to the medium and immediately filtered, as the amount of foreign matter adsorbable in the concentrated medium increases.

Precipitation is carried out in a selected beaker filled to the maximum of 2/3 of the cabinet at the end of the total volume treatment. The addition of the precipitation reagent is done with burette, pipette and occasionally gauge vessel. Mixing is usually done with a bagel 3-4 cm longer than the beaker's height. Mechanical or magnetic stirrer is used for long mixing time.

1.2. Digestion

The precipitates in the crystal structure usually do not leak immediately. In its own case or in the water bath, it is left for 3-4 hours or overnight. This process is called maturation.

During precipitation, large crystals as well as very small crystals occur. The solubility of small crystals is higher than that of large crystals. Small crystals dissolve during standby. On the surface of larger crystals accumulation occurs and large crystals are obtained.

In addition to facilitating filtration, Digestion also allows precipitation to be purified.

1.3. Filtration

The black tape has large size pores, and the paper symbols. The filter paper is inserted well into the hopper dry. The air bubbles between the funnel and the paper are removed when the distill is filled with water and is expected to be filtered. The droplet of dripping filtrate is placed in contact with the edge of the beaker.

The filtered liquid is carefully transferred to the filter paper without initially mixing to prevent plugging of the pores. To prevent material loss by splashing, the drained fluid is transferred from the beaker in the beaker onto a bagel which is held in the middle of the funnel but does not come into contact with the funnel. The filter paper should not be completely filled with liquid. It should be 5 mm below the upper edge of the paper. After the entire liquid is transferred, the beaker is washed with distilled water and the wash water is transferred to the filter paper.

The precipitate should not cover more than half of the filter paper. Otherwise it can not be washed well.

Filters outside the paper are used to filter precipitates that are easily reduced during heating or only weighed by drying.

1.4. Washing

On the surface of the precipitate, washing is carried out to remove foreign ions adsorbed and the main solvent.

In the case of washing with pure water, depending on the structure of the precipitate, losses may occur due to dissolution, colloidal formation and hydrolysis. Washing solutions are used to prevent this.

Washing solutions are collected in three groups:

1) Solvents that precipitate in water to dissolve by ionization: These are solutions containing common ions with the precipitate. The co-ion can easily be given in the form of a solution of a volatile compound or precipitate.

For example, the $Fe(OH)_3$ precipitate can be washed with the NH_4OH solution.

2) Solvents that prevent the dissolution of precipitate by giving colloidal solution: When precipitation is provided by the addition of coagulant, this electrolyte is removed during washing with water and the colloidal solution comes back to the water. In this case, washing is

carried out with dilute electrolyte solution. During washing, the ions contained in the wash solution are replaced by foreign ions adsorbed by the precipitate. For this purpose, the ammonium salt, acid dissolving, etc. used. For example, $Fe(OH)_3$, ammonium salt solution; AgCl is washed with 1% HNO_3 solution.

3) Solvents which inhibit the hydrolysis of the precipitate: Some precipitates are lost in water washing due to hydrolysis. For example, magnesium ammonium phosphate precipitate,

$$MgNH_4PO_4 + H_2O \rightleftharpoons MgHPO_4 + NH_4OH$$
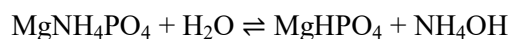
In the form of hydrolysis. NH_4OH is added to the wash water to prevent this.

If the formation of ionizing colloidal solution is not lost due to reasons such as hydrolysis, it is washed with distilled water.

Washing process:

In the filter wash, a certain amount of washing solution or distilled water is added to the precipitate. Once all of this has been filtered, another portion is added. The same volume is more effective than using washing liquid in small portions.

In another wash, the precipitate is taken up in a beaker and a certain amount of washing liquid is added thereto, followed by stirring. After the sediment is settled to the bottom of the beaker, filtration is carried out. This method is more effective in eliminating pollution since foreign substances in the sediment dissolve to the fullest extent.

In both washings, the washing is continued until the foreign matter desired to be purified from the precipitate is not found in the filtrate.

If the solubility of the precipitate is low, the hot liquid is preferred in washing, since it will increase the solubility of the foreign substances and the filtration will be faster due to the decrease in viscosity.

1.5. Drying and Igniting

The washed precipitate is washed with water or the like before weighing. It is dried or pissed to get the volatile substances out. During the glow process, the composition of the precipitate may remain the same or change. For example, while the structure of $BaSO_4$ remains the same in the glow process, the $MgNH_4PO_4$ precipitate turns into $Mg_2P_2O_7$ form. If the required temperature is less than 250 ^{o}C, the drying process is irritating if it is between 250 and 1200 ^{o}C. The drying

process is carried out in the body, the glowing oven or the burner. Dried sediment is filtered through filter paper, Gooch crucible, sintered glass or die bore porous porcelain crucible.

If the precipitate is incinerated, filter paper, dia pore porcelain or silica crucible or Munroe crucible is used for filtration.

Fixed scales are brought to the crucible before drying or glowing. For this, the crucible is heated at the drying or glowing temperature. It is cooled and weighed by taking the desiccator with the help of a pliers or wire tongs. The crucible is reheated and weighed. If the difference between the two weights does not exceed 0,0001 g, it is assumed that the croissant has reached a fixed level of digestion. Otherwise, the process is repeated.

When filtration is done using strainer paper, the edges are folded with the help of a moist strainer paper pens and then the crucible is brought to a fixed weighing scraper so that the sharp tip remains at the top. The crucible is first placed obliquely on the asbestos wire with clay triangle. The crucible is occasionally twisted and the filter paper is heated to dryness. After the drying is completed, the asbestos wire is lifted and the paper is heated by heating directly in the flame. At this time, either the crucible is heated from the side or it is placed obliquely on the clay triangle to provide the necessary air flow for combustion. If the paper flames during the burning, the crucible is turned off by flicking it with the watch glass. After stopping the smoke outlet, put the crucible metal oven tongs in the constant temperature ash furnace and heat it for 12-15 minutes.

It is cooled and weighed by taking the desiccator with wire tongs or pens again. Coke is reheated and weighed with the substance. If the difference between the two weights does not exceed 0.0001 g, it is assumed that the weight is constant. Otherwise, the glowing and weighing process is repeated.

Note: 1) After the drying and burning process, the crucible should not be held until weighing.

2) If the substance to be weighed is excessive moisture, the cover is used between cooling and weighing.

1.6.Weighing

In gravimetric analysis, weighing is carried out on a double or single-pan balance with a sensitivity of at least 0.0001 grams. It is recommended to weigh empty and full crucible on the same balance. During material weighing, since there will be difference between full and empty crucible, there will be no error from the balance.

During weighing:

1. Non-cooled crucible should not be put on the balance.
2. The lids should be closed before the balance is turned to the weighing position.
3. First, approximate weigh should be found in rough weighing position, and then sensitive weighing should be carried out.
4. When the balance is in weighing position, the crucible should not be put on or taken to the pan.
5. Before weighing, the balance is checked whether it is at zero level (balanced) or not and it should be adjusted if necessary.
6. Whether the bottom of the balance is properly in a horizontal position should be controlled from water level on the balance.
7. In the balance, there should be desiccant substances such as silica gel, anhydrous $CaCl_2$, NaOH and so on.

1.7. Calculation of Result

In the calculation of the result, regardless of the steps followed during the analysis, it is sufficient to use only the sought and weighed substance formulas. It is recommended that the amount of substance to be weighed is 0.1-0.5 g. The increase in the amount of the substance reduces the error rate in the analysis. When writing the calculated result, the last digit should be the first suspected number. In the student laboratory, four numbers after the comma should be written.

Example: For the determination of sodium sulphate, the sulphate in solution is precipitated by adding $BaCl_2$ solution. After it is filtered and washed, it is weighed by heating. In $BaSO_4$ weighing, if T is gram, the amount of sulphate in the solution is calculated as follows:

Crucible weight with precipitate - empty crucible weight = T (amount of $BaSO_4$)

While;

233 g $BaSO_4$ is formed by 142 g Na_2SO_4

T g $BaSO_4$ is formed by X g Na_2SO_4

$X = \frac{142}{233} x\, T$ g Na_2SO_4

Formerly, 142/233 ratio in the equation obtained as a result of ratio is called gravimetric factor and these values took place in analytical chemistry charts. This equation, which is basically

expressed as a formula, is the result of a simple ratio and it is not necessary to be used by memorizing.

1.8. Iron-Manganese Separation

One of the important processes in the analysis of glass, cement, mineral, alloy etc. is the separation of divalent cations from higher valence cations. In this separation, it is benefited from the fact that the precipitation pHs of the metal hydroxides are different. The precipitation pHs of some metal-hydroxides are given in the following table:

pH	Metal Ion
2	Ti^{4+}, Zr^{4+}
3	Sn^{2+}, Fe^{3+}
4	Th^{4+}
5	Al^{3+}
6	Zn^{2+}, Cu^{2+}, Cr^{3+}
7	Fe^{2+}
8	Co^{2+}, Ni^{2+}, Cd^{2+}
9	Ag^+, Mn^{2+}, Hg^{2+}
11	Mg^{2+}

In the analysis reports, the metal oxide mixture weighed after the hydrocarbons of Fe^{3+}, Al^{3+}, Ti^{4+}, Zr^{4+} cations are separated and heated is given as R_2O_3.

For separation by precipitation in the form of hydroxide, weak bases are used. Ammonium hydroxide, acetate and benzoate salts, urea, pyridine, urotropine are used as weak bases. Ammonium hydroxide and acetate salts among them are widely used. As ammonium hydroxide may contain carbonate and silicate, it causes divalent cations to precipitate partially.

Furthermore, if it is not added to the medium, pH rising causes aluminum hydroxide to precipitate as aluminate. Such problems are not seen in precipitation by acetate.

Since the metal hydroxides, which are precipitated by weak bases, are voluminous and gelatinous, they adsorb ions in the solution. For this reason, it is recommended to filter and dissolve the solution in acid, to precipitate it again and to combine the filtrates.

This method will be applied in the student laboratory since ammonium hydroxide precipitation is used more often.
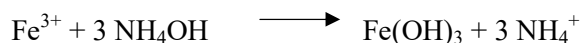
During the precipitation of Fe^{3+} ions with NH_4OH, other cations precipitated in the form of hydroxides are also separated together. For example; Al^{3+}, V^{3+}, Ti^{4+}, Zr^{4+} and so on. The medium should be buffered by adding the ammonium salt to prevent the precipitation of ions such as Mg^{2+}, Mn^{2+}, Zn^{2+} and so on, which precipitate in the form of hydroxides at relatively high ph. Since NH_4Cl will cause iron loss by forming volatile $FeCl_3$ during heating, NH_4NO_3 should be used instead of NH_4Cl or precipitation should be thoroughly washed with NH_4NO_3 solution. If Al^{3+} ion is present in the medium, it should be avoided to add excess NH_4OH in order to separate it quantitatively with Fe^{3+} in the form of hydroxide. Because it causes $Al(OH)_3$ to partially dissolve in aluminate form. Furthermore, the presence of substances such as hydroxyl acids, polyalcohols, phosphates, fluorides and so on, which complexes with Fe^{3+} prevents the quantitative precipitation of iron.

1.9. Gravimetric Determination of Iron

Take your sample which is provided in a 100 mL volumetric flask and add distilled water till the its mark. Shake the solution well and transfer 25.0 mL of sample solution with pipette into a beaker. Add about 100 mL of distilled water and heat the solution on a hot plate to about 90-100°C. Boiling the solution must be avoided since it is possible to lose some of the solution through spattering. However, it is necessary to keep the solution at an elevated temperature in order to facilitate the formation of large, filterable particles and to minimize coprecipitation of foreign ions. After boiling gently for 1 min, add diluted NH_4OH solution (1:1, v/v) dropwise until pH reaches 7 in order to precipitate Fe^{3+} ions in the form of $Fe(OH)_3$. Allow the precipitate to settle, and test for completeness of precipitation by adding a few more drops of NH_4OH. If you detect the appearance of some red-brown precipitate as the drop of the solution moves downward through the solution add an additional NH_4OH solution (control the pH.) The reaction is:

$$Fe(H_2O)_6^{3+} + 3\ NH_3 \longrightarrow Fe(H_2O)_3(OH)_3 + 3\ NH_4^+$$

in simple terms;

$$Fe^{3+} + 3\ NH_4OH \longrightarrow Fe(OH)_3 + 3\ NH_4^+$$

Decant the supernatant liquid through a black band filter paper. Wash the precipitate several times with hot 1% NH_4NO_3 solution (The filtrate must be kept for determination of manganese). Remove the filter paper with precipitate and then place it in a crucible taken to

the constant weight. Dry the paper with a small flame and heat the crucible for 15 min at 500 – 550 $^{\circ}$C on an electric furnace for ignition. Allow to coll in a desiccator and weigh Fe_2O_3.

$$2\ Fe(OH)_3 \longrightarrow Fe_2O_3 + 3\ H_2O$$
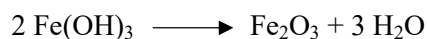
Note: Total iron in the sample must be in the form of Fe^{3+} If not, 1-2 mL of con. HNO_3 or H_2O_2 are added to the sample and so iron is oxidized.

Calculations:

$$Fe^{3+} + 3\ NH_4OH \longrightarrow Fe(OH)_3 + 3\ NH_4^{+}$$

$$2\ Fe(OH)_3 \longrightarrow Fe_2O_3 + 3\ H_2O$$

T (Fe_2O_3) = $m_{\text{crucible with precipitate}}$ - m_{crucible}

T g Fe_2O_3 . $\dfrac{1\ \text{mol } Fe_2O_3}{160\ \text{g } Fe_2O_3}$. $\dfrac{2\ \text{mol } Fe^{3+}}{1\ \text{mol } Fe_2O_3}$. $\dfrac{56\ \text{g } Fe^{3+}}{1\ \text{mol } Fe^{3+}}$. $\dfrac{100\ \text{mL}}{25\ \text{mL}}$

$= \dfrac{112}{160}$ **x T** X 4 g Fe^{3+}/100 mL

II. Solution Route:

T (Fe_2O_3) = $m_{\text{crucible with precipitate}}$ - m_{crucible}

While,

160 g Fe_2O_3	is formed by 2x56 g Fe^{3+}	(Fe: 56 g/mol)
T g Fe_2O_3	is formed by A g Fe^{3+}	(Fe_2O_3 : 160 g/mol)

A = $\dfrac{112}{160}$ **x T** g Fe^{3+}

While,

25 mL of sample   contain A x 10^3 mg Fe^{3+}

100 mL of sample   contain ? mg Fe^{3+}

The result is found as mg/100 mL

1.10. Gravimetric Determination of Manganese

Add 4 spoon of NH_4Cl ve 2 spoon of $(NH_4)_2HPO_4$ to the previous filtrate. Heat the solution to 90 – 95 $^{\circ}$C and then add diluted NH_4OH (1:3, v/v) until pH is 9. Continue to heat for a while and settle it on the water bath for 1-2 h for digestion.

$Mn^{2+} + HPO_4^{2-} + NH_4OH \longrightarrow MnNH_4PO_4.H_2O$

Filter through a blue band filter paper. Wash the precipitate several times with cold 1% NH_4NO_3 solution. Remove the filter paper with precipitate and then place it in a crucible taken to the constant weight. Dry the paper with a small flame and heat the crucible for 15-20 min at $700 - 800 \,^{\circ}C$ on an electric furnace for ignition. Allow to coll in a desiccator and weigh $Mn_2P_2O_7$.

$2\ MnNH_4PO_4.H_2O \longrightarrow Mn_2P_2O_7 + 2NH_3 + 3H_2O$

Calculations:

$Mn^{2+} + HPO_4^{2-} + NH_4OH \longrightarrow MnNH_4PO_4.H_2O$

$2\ MnNH_4PO_4 . H_2O \longrightarrow Mn_2P_2O_7 + 2\ NH_3 + 3\ H_2O$

$T\ (Mn_2P_2O_7) = m_{crucible\ with\ precipitate} - m_{crucible}$

$T\ g\ Mn_2P_2O_7 \ . \ \dfrac{1\ mol\ Mn_2P_2O_7}{284\ g\ Mn_2P_2O_7} \ . \ \dfrac{2\ mol\ Mn^{2+}}{1\ mol\ Mn_2P_2O_7} \ . \ \dfrac{55\ g\ Mn^{2+}}{1\ mol\ Mn^{2+}} \ . \ \dfrac{100\ mL}{25\ mL}$

$= \dfrac{110}{284}\ x\ T \ X\ 4\ \ g\ Mn^{2+}/100\ mL$

II. Solution Route:

$T\ (Mn_2P_2O_7) = m_{crucible\ with\ precipitate} - m_{crucible}$

While,

284 g $Mn_2P_2O_7$	is formed by 2x55 g Mn^{2+}	(Mn: 55 g/mol)
T g $Mn_2P_2O_7$	is formed A g Mn^{2+}	($Mn_2P_2O_7$: 284 g/mol)

$A = \dfrac{110}{284}\ x\ T\ g\ Mn^{2+}$

While,

25 mL of sample   contain $A\ x\ 10^3$ mg Mn^{2+}

100 mL of sample   contain ? mg Mn^{2+}

The result is found as mg/100 mL.

2. VOLUMETRY (TITRIMETRY)

Volumetry is an analytical method based on the measurement of solution volume consumed in the reaction of solution with known concentration of solution of substance to be analyzed and another substance capable of reacting with this substance. Because the process is based on titration, it is also called **titrimetry.**

In order for a reaction to be used in volumetric analysis,

1. Reaction should be expressed by a single and simple equation.

2. Reaction should be fast enough.

3. At the point where the reaction called the equilibrium point is completed, the observable physical or chemical change should occur. If this does not occur, the substances that show observable change at equivalent points and that are called indicators should be used.

4. The amount of substance balanced in the equivalent point should be at most 1/1000 of the initial amount.

In titrimetric analysis, the solution with known concentration is called **standard solution, adjusted solution or titrant**, the substance that is titrated with the standard solution and the amount is desired to be determined is called **analyte**. The standard solution, which is usually filled in the buret, is added drop by drop to the solution containing the substance to be analyzed in Erlenmeyer. At this time, the Erlenmeyer containing analysis solution is mixed by shaking and the reaction is allowed to take place everywhere. The upper limits of the standard solution in buret are read before process begins and after the reaction is completed. The difference between two levels is found as the volume used for titration (V). Due to the affinity between glass and water molecules, the surface of the solution in the buret is spherical. Volume reading is performed considering the tangent at the lowest point of the spherical surface in colorless solutions and the uppermost part in colored solutions.

To measure the volume of the consumed solution, liter (L) as basic unit of volumetric measurement for liquids or its submultiples (usually milliliter, mL) is used. 1 L is the volume of 1 kg (in the air) consumed water at 4 °C.

Standard solutions at the appropriate dilution and concentration should be used to reduce errors during titration. Depending on the amount of the substance titrated, solutions with concentrations of 1.0 M, 0.1 M, 0.01 M, etc. are usually used. Furthermore, conventional

solutions containing 1 mg/mL analyte and giving the amount of the analyte directly in mg can also be prepared after titration to provide ease calculation.

Standard solutions prepared to be 0.1 M, 0.05 M, 0.01 M etc., cannot be prepared at the exact desired concentration due to reasons such as impurities, weighing errors or decay. Either more concentrated or more diluted solutions than desired are obtained. Therefore, in order to find the actual concentration of the standard solution, the prepared solution should be titrated with the amount of a pure substance (primer standard) weighed sensitively or a specific volume of another solution (secondary standard) with known concentration.

In a volumetric analysis, the process is completed when the standard solution in an amount equivalent to the titrated substance reacts. In order to determine this equivalence point, an indicator appropriate to the medium should be added. At the end of the titration (at the turning point), the amount of standard solution consumed is read from buret. Since the actual concentration of the standard solution is also known, the amount of the substance in it is easily calculated. Since the amount of the standard solution and the amount of the analyte substance are equal in this time, the quantitation of the analyte can be calculated.

Volumetric analyzes are divided into four basic groups, considering the type of reaction occurring during titration:

1) **Neutralization Titrations**
   a) Acidimetry
   b) Alkalimetry

2) **Redox Titrations**
   A) Oxidimetry (Oxidation-based methods)
   a) Manganometry
   b) Bromometry
   c) Serimetry
   d) Iodometry
   e) Chromometry
   f) Oxidation with iodate
   B) Reductimetry (Reduction-based methods)
   a) Titanometry
   b) Iodometry
   c) Reduction with Hipovanadate

d) Reduction with Chromium (II)

3) Precipitation Titrations

4) Complexometric Titrations

2.1. Neutralization Titrations

They include volumetric analyzes, in which the neutralization reactions occur. The determination of the base amount in the sample by titrating with standard acid solution is called "acidimetry", the determination of the acid amount in the sample with base solution is called "alkalimetry". The equivalent point of neutralization titrations is determined by the aid of color-changing indicators at a specific pH or potentiometric method.

2.1.1. Acidimetry

Since most of the cations are easily dissolved in water, HCl solution is usually used in the titration. H_2SO_4 solution is used in the presence of chlorine oxidizing agents or it is used when long heating is required.

Preparation of 0.1 M Hydrochloric Acid Solution

Hydrochloric acid is commonly available as a concentrated aqueous solution containing about 37% (w/w) HCl.

Mw: 36.5 g/mol

d_{HCl}= 1.19 g/mL

Mass percentage (w/w): 37%

$$V \text{ mL HCl} = \frac{0.1 \text{ mol HCl}}{1.0 \text{ L HCl}} \cdot \frac{36.5 \text{ g HCl}}{1 \text{ mol HCl}} \cdot \frac{100 \text{ g}}{37 \text{ g}} \cdot \frac{1 \text{ mL}}{1.19 \text{ g}} = 8.29 \text{ mL}$$

II. Solution Route:

While,

| 1 mole HCl | is 36.5 g |
| 0.1 mole HCl | is X g |

X= 3.65 g HCl

| 100 g of HCl solution | have 37 g HCl, then |
| X g of HCl solution | have 3.65 g HCl |

 X= 9.86 g of HCl solution is required.

| 1 mL of HCl solution | is 1.19 g |
| X mL of solution | is 9.86 g |

X= 8.29 mL

HCl acid volume calculated is transfered into a volumetric flask, then diluted until 1.0 L with distilled water and mix well.

Standardization of 0.1 M HCl Solution

Since the exact concentration of the concentrated HCl reagent solution cannot be reliably known (the gas fumes out of the solution all the time), the exact concentration of HCl solution is determined by titration with primary or secondary standard chemicals. This solution is to be standardized using anhydrous Na_2CO_3, $NaHCO_3$, $Na_2B_4O_7$, HgO or tiosulphate solutions.

Sodium carbonate is frequently used as a standard material for acid solutions.

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$
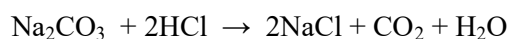
Accurately weigh out three 0.1 g samples of dried, anhydrous Na_2CO_3 directly into separate, clean and dry 250 mL conical flasks. Add 50 mL of distilled water to dissolve the carbonate. Rinse 50 mL buret with small portions of your HCl solution and then fill it with the acid solution (record the initial reading). Add 3-5 drops of methyl orange as an indicator to the flask. Carry out a titration by adding the HCl solution prepared from the burette to the conical flask, swirling the flask constantly, until the solution just changes its color from yellow to red. Repeat the titration three times and find the average of volumes. Calculate the real concentration of the HCl solution and write its molar concentration founded on label.

Calculations:

Two end points are observed in the titration of sodium carbonate:

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$

$$NaHCO_3 + HCl \rightarrow H_2CO_3 + NaCl$$
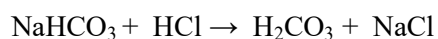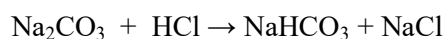
Specimen results:

Average of accurate titres: 10.0 mL

Weight of Na_2CO_3= 0.0500 g

$$0.0500 \text{ g Na}_2\text{CO}_3 = 10.0 \text{ mL HCl} \cdot \frac{X \text{ mol HCl}}{1000 \text{ mL HCl}} \cdot \frac{1 \text{ mol Na}_2\text{CO}_3}{2 \text{ mol HCl}} \cdot \frac{106 \text{ g Na}_2\text{CO}_3}{1 \text{ mol Na}_2\text{CO}_3}$$

X= 0.0943 M HCl, real concentration of hydrochloric acid solution.

II. Solution Route:

106 g Na$_2$CO$_3$ is 1 mole

0.0500 g   is X mole.

X= 4.72×10^{-4} mole Na$_2$CO$_3$

According to the reaction above;

1 mole Na$_2$CO$_3$ react with 2 mole HCl

4.72×10^{-4} mole   Na$_2$CO$_3$ react with X mole HCl.

X= 9.43×10^{-4} mol HCl

10.0 mL of HCl solution   contain 9.43×10^{-4} mole HCl, so

1000 mL of HCl solution   contain X mole HCl.

X= 0.0943 mol/L HCl

2.1.1.1. Determination of Sodium Hydroxide-Sodium Carbonate

A. Take your sample which is provided in a 100 mL volumetric flask and add distilled water till the its mark. Shake the solution well and transfer duplicate 25.0 mL samples with pipette into two separate conical flasks. Dilute the samples to 75-100 mL with distilled water. Add 3-5 drops of phenolphthalein indicator (pink color occurs, pH: 8.3). Titrate with standardized HCl solution until the indicator turns colorless. Record the titrant volume where the indicator changes color (V$_1$).

NaOH + HCl → NaCl + H$_2$O
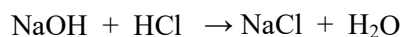
if the volume of HCl solution used in this titration; X mL and

Na$_2$CO$_3$ + HCl → NaHCO$_3$ + NaCl
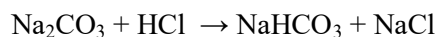
the volume of HCl solution used in this titration; Y mL, then

V$_1$ = X + Y

Take another sample containing 25.0 mL of the unknown solution, add 3-5 drops of methyl orange indicator (yellow-orange color, pH: 3.1 - 4.7) and carry the titration until the color turns into red. Boil the solution gently and drive off CO_2. Cool the solution to room temperature under the tap water and carry on the titration till you reach the red end-point. Record again the titrant volume where the indicator changes color (V_2).

$$NaOH + HCl \rightarrow NaCl + H_2O$$

if the volume of HCl solution used in this titration; X mL,

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$
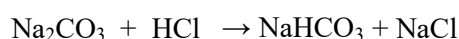
the volume of HCl solution used in this titration; Y mL and

$$NaHCO_3 + HCl \rightarrow H_2CO_3 + NaCl$$
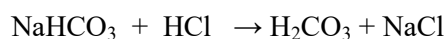
again the volume of HCl solution used in this titration; Y mL. Because the mole number of Na_2CO_3 equals to the mole number of $NaHCO_3$, they require the same volume of HCl solution. If so;

$$V_2 = X + Y + Y$$

Calculations:

In order to titrate NaOH and Na_2CO_3, volumes of standardized HCl solution required:

$V_{NaOH} = V_1 - (V_2 - V_1)$ mL $\{ V_{NaOH} = (X + Y) - [(X + Y + Y) - (X + Y)] \}$

$V_{NaOH} = X\ mL$

and

$V_{Na2CO3} = 2 \times (V_2 - V_1)$ mL $\{ V_{Na2CO3} = 2 \times [(X + Y + Y) - (X + Y)] \}$

$V_{Na2CO3} = 2Y\ mL$

M_{HCl}= 0.1000 M

Mw_{NaOH}= 40 g/mol

Mw_{Na2CO3}= 106 g/mol

? m NaOH= X mL HCl . 0.1000 mol HCl . 1 mol NaOH . 40 g NaOH . 100 mL

                            1000 mL HCl   1 mol HCl   1 mol NaOH   25 mL

? m Na$_2$CO$_3$= 2Y mL HCl . <u>0.1000 mol HCl</u> .<u>1 mol Na$_2$CO$_3$</u> . <u>106 g Na$_2$CO$_3$</u> . <u>100 mL</u>

$$\qquad\qquad\qquad\qquad\text{1000 mL HCl}\qquad\text{2 mol HCl}\qquad\text{1 mol Na}_2\text{CO}_3\qquad\text{25 mL}$$

II. Solution Route:

The mole number of NaOH:

n_{HCl} = M_{HCl} . V_{HCl} = 0.1000 . X = A mmol HCl

At the end-point, the mole number of HCl equals to the mole number of NaOH; A mmol.

While,

1 mmol NaOH	is 40 mg	If 25 mL of sample	contain 40A mg of NaOH,
A mmol NaOH	is 40A mg.	100 mL of sample	contain 160A mg of NaOH.

The mole number of Na$_2$CO$_3$:

n_{HCl} = M_{HCl} . V_{HCl} = 0.1000 . 2Y = B mmol

At the end-point, for B mmol HCl, there is B/2 mmol Na$_2$CO$_3$. Because 2 mol HCl react with 1 mol Na$_2$CO$_3$ according to the neutralization reaction.

1 mmol Na$_2$CO$_3$	is 106 mg	If 25 mL of sample	contain 53B mg of Na$_2$CO$_3$,
B/2 mmol Na$_2$CO$_3$	is 53B mg.	100 mL of sample	contain 4 x 53B mg of Na$_2$CO$_3$.

Report the results in terms of mg of analyte per 100 mL of sample.

B. Only one sample can be used for the titration of these analytes. Take a 25 mL portion of sample, add 3-5 drops of phenolphthalein indicator and titrate the sample with standard HCl until the indicator turns colorless. Record the titrant volume where the indicator changes color (V$_1$). Afterwards, add 3-5 drops of methyl orange indicator and perform the titration until the color turns into red. Again, note the HCl volume where methyl orange indicator changes color (V$_2$).

The volumes of HCl solution required for analytes can be calculated as showed below:

V_{NaOH} = V_1 − V_2 mL   { V_{NaOH} = (X + Y) –(Y) }

V_{NaOH} = X   mL   and

V_{Na2CO3} = 2 x V_2 mL   { V_{Na2CO3} = 2 x Y }

V_{Na2CO3} = 2Y   mL

Similarly, the amounts of the analytes can be calculated as described above.

2.1.2. Alkalimetry

Standard base solutions are prepared using NaOH, KOH or $Ba(OH)_2$. Because it is cheap, the most used base solution is NaOH. However, due to its dissolution in alcohol, KOH is used for titration in alcoholic medium and $Ba(OH)_2$ solution is used for titration of organic acids.

Preparation of 0.1 M Sodium Hydroxide Solution

Solid NaOH is highly hygroscopic (it absorbs water from the air) and thus it cannot be accurately weighed. It also absorbs carbon dioxide from the air, forming sodium carbonate and thereby reducing the amount of sodium hydroxide present. This means that a NaOH solution of known molarity cannot be directly prepared without resorting to an air-and-water-free environment. In cases like this we need to use an acid as the primary standard (potassium hydrogen phthalate) or an acid solution as the secondary standard (standardized HCl solution) to determine the exact concentration of the NaOH solution.

NaOH quantity (m_{NaOH}, g), which is required to prepare 1.0 L 0.1 M solution, is calculated as follows:

$$m_{NaOH} = \underline{0.1 \text{ mol NaOH}} \quad . \quad \underline{40 \text{ g NaOH}}$$
$$1 \text{ mol NaOH}$$

$$m_{NaOH} = \textbf{4 g } NaOH$$

Weigh out 4 g NaOH and dissolve the base in some distilled water. Then transfer the solution to 1.0 L volumetric flask and make up the volume to 1.0 L with distilled water.

Standardization of 0.1 M NaOH Solution using a Standard Solution of HCl

Pipette 10.0 mL of standardized HCl solution into a flask and add 3-4 drops of methyl orange or phenolphthalein indicator. Fill the burette with NaOH solution prepared and the titrant is slowly added to the solution being titrated until the indicator changes color. Repeat the titration with at least three samples, record the average off all titrations and calculate the real molarity of the NaOH solution as stated below. Record the value on the bottle lable.

$$M_{HCl} . V_{HCl} = M_{NaOH} . V_{NaOH}$$

2.1.2.1. Determination of Phosphoric Acid-Disodium Hydrogen Phosphate

Although phosphoric acid often listed together with strong mineral acids (hydrochloric, nitric and sulfuric) it is relatively weak, with $pKa_1 = 2.15$, $pKa_2 = 7.20$ and $pKa_3 = 12.35$. That means titration curve contains only two inflection points and phosphoric acid can be titrated either as a monoprotic acid or as a diprotic acid. In the first case acid has to be titrated against indicator changing color around pH 4.7 (for example methyl orange), in the second case - against indicator changing color around pH 9.6 (for example thymolphthalein). Phenolphthalein can't be used for only H_3PO_4, as it starts to change color around pH 8.2, when phosphoric acid is titrated in about 95%.
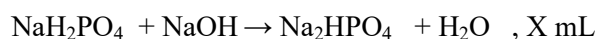
Transfer 25.0 mL sample with pipette into a conical flask. Dilute the sample to 75-100 mL with distilled water. Add 3-4 drops of methyl orange indicator. Titrate with standardized NaOH solution till the first color change. Record the titrant volume where the indicator changes color (V_1).

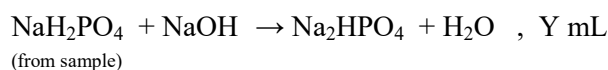$$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$$
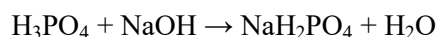
if the volume of NaOH solution used in this titration; X mL, then

$$V_1 = X \text{ mL}$$

Take another sample containing 25 mL of the sample solution, add 3-4 drops of phenolphthalein indicator and carry out the titration until the color turns into pink. Record again the titrant volume where the indicator changes color (V_2).

$$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O \quad , \quad X \text{ mL}$$

$$NaH_2PO_4 + NaOH \rightarrow Na_2HPO_4 + H_2O \quad , \quad X \text{ mL}$$

$$\mathbf{V_{H3PO4}} = X + X = 2X \text{ mL,}$$

$$NaH_2PO_4 + NaOH \rightarrow Na_2HPO_4 + H_2O \quad , \quad Y \text{ mL}$$
(from sample)

$$\mathbf{V_{NaH2PO4}} = Y \text{ mL}$$

$$\mathbf{V_2} = \mathbf{V_{H3PO4}} + \mathbf{V_{NaH2PO4}}$$

$$V_2 = 2X + Y$$

Calculations:

In order to titrate H_3PO_4 and NaH_2PO_4, volumes of standard NaOH solution required:

$V_{H3PO4} = 2V_1 = 2X$ mL ,

$V_{NaH2PO4} = V_2 - 2V_1 = (2X + Y) - 2X = Y$ mL

The amounts of the analytes can be calculated as follows:

$M_{NaOH} = 0.1000$ M

$Mw_{H3PO4} = 98$ g/mol

$Mw_{NaH2PO4} = 120$ g/mol

? m H_3PO_4 = 2X mL NaOH . $\underline{0.1000\ mol\ NaOH}$. $\underline{1\ mol\ H_3PO_4}$. $\underline{98\ g\ H_3PO_4}$. $\underline{100\ mL}$
          1000 mL NaOH   2 mol NaOH   1 mol H_3PO_4 25 mL

? m NaH_2PO_4= Y mL NaOH. $\underline{0.1000\ mol\ NaOH}$. $\underline{1\ mol\ NaH_2PO_4}$. $\underline{120\ g\ NaH_2PO_4}$. $\underline{100mL}$
          1000 mL NaOH   1 mol NaOH   1 mol NaH_2PO_4 25mL

II. Solution Route:

The mole number of H_3PO_4:

$n_{NaOH} = M_{NaOH}$. $V_{NaOH} = 0.1000$. $2X = A$ mmol NaOH

At the end-point, for A mmol NaOH, there is A/2 mmol H_3PO_4.

| 1 mmol H_3PO_4 | is 98 mg | If 25 mL of sample | contain 49A mg H_3PO_4, |
| A/2 mmol H_3PO_4 | is 49A mg. | 100 mL of sample | contain 4 x 49A mg H_3PO_4. |

The mole number of NaH_2PO_4:

$n_{NaOH} = M_{NaOH}$. $V_{NaOH} = 0.1000$. $Y = B$ mmol NaOH

At the end-point, the mole number of NaOH equals to the mole number of NaH_2PO_4; B mmol.

While,

| 1 mmol NaH_2PO_4 | is 120 mg | If 25 mL of sample | contain 120B NaH_2PO_4, |
| B mmol NaH_2PO_4 | is 120B mg. | 100 mL of sample | contain 4 x 120B mg NaH_2PO_4. |

Report the results in terms of mg of analyte per 100 mL of sample.
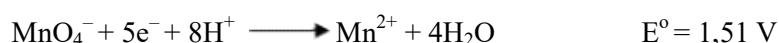
2.2. Redox Titrations

When electrons are transferred from one atom to another in the substances reacting during a reaction, such reactions are called redox reactions. In a redox reaction, the element-losing electron is oxidized, while the element-gaining electron is reduced. The substances containing an element that losses electron are defined as reducing agent, the substances containing an element that gains electron are defined as oxidizing agent. A substance in the low oxidation step in the solution is converted to the compound in the higher oxidation step by reacting with an oxidizing agent. The amount of reducing agent is calculated using the concentration of the oxidizing agent solution and the volume consumed in the titration. Similar calculations apply for the amount of oxidizing agent.

Titrations performed by oxidation and reduction reactions are called redox titration. If the solution used in the titration is an oxidizing agent solution, the analytical method is called oxidimetry, if the solution used in the titration is a reducing agent solution, the analytical method is called reductimetry.

2.2.1. Manganometry

Redox titrations using potassium permanganate are called manganometry. Potassium permanganate is a strong oxidizing. Depending on pH of the medium, the reactions can be as follows:

a) In strong acidic mediums

$$MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O \qquad E^o = 1,51 \text{ V}$$

b) In weak acidic, weak basic and neutral mediums

$$MnO_4^- + 3e^- + 2H_2O \longrightarrow MnO_2 + 4OH^- \qquad E^o = 1,70 \text{ V}$$

c) In strong basic mediums

$$MnO_4^- + e^- + 2H_2O \longrightarrow MnO_4^{2-} \qquad E^o = 0,56 \text{ V}$$

The permanganate solution is one of the most preferred solutions for redox titrations, due to the reasons such as the ability to oxidize even weaker reducing agents and no need for an indicator to show the turning point during titration.

Preparation of 0.02 M Potassium Parmanganate Solution

Weigh out 3.16 g of $KMnO_4$ (Mw: 158 g/mol) and dissolve it in 1.0 L of distilled water. Heat to boiling and keep hot for about 15-30 min. After cooling, filter the solution through a fine-porosity filtering crucible. Transfer the solution to a clean glass-stoppered dark bottle and keep away from sunlight.

Standardization of 0.02 M $KMnO_4$ Solution with Sodium Oxalate

As_2O_3, KI, iron wire, $K_4[Fe(CN)_6].3H_2O$, $Na_2C_2O_4$ or $H_2C_2O_4.2H_2O$ can be used to determine the exact concentration of the $KMnO_4$ solution.

Dry $Na_2C_2O_4$ for at least 1 h at 105-110 ^0C and cool in a desiccator. Dissolve 0.1 g of the dried $Na_2C_2O_4$ in 50 mL of distilled water in a conical flask. Transfer 10.0 mL of 1.0 M H_2SO_4 solution and heat the content of the flask up to 80-90 °C. Titrate until the single drop of potassium permanganate is enough for the solution to get purple. If the amount of acid is not enough, brown precipitate of MnO_2 can be formed. Repeat the titration with at least three samples, record the average off all titrations and calculate the real molarity of the $KMnO_4$ solution as stated below. Record the value on the bottle lable.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2\ Mn^{2+} + 10\ CO_2 + 8\ H_2O$$
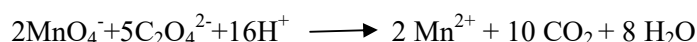
Calculations:

Chemical reaction above is observed in the titration of $Na_2C_2O_4$ with $KMnO_4$ under acidic conditions.

Specimen results:

Average of accurate titres (V_{KMnO_4}): 15.0 mL

Weight of $Na_2C_2O_4$ = 0.1000 g

0.1000 g $Na_2C_2O_4$ = 15.0 mL $KMnO_4$. $\underline{\textbf{X mol } KMnO_4}$. $\underline{\text{5 mol } Na_2C_2O_4}$. $\underline{\text{134 g } Na_2C_2O_4}$
 1000 mL $KMnO_4$ 2 mol $KMnO_4$ 1 mol$Na_2C_2O_4$

X= 0.0198 M $KMnO_4$, real concentration of the solution.

II. Solution Route:

While,

134 g $Na_2C_2O_4$ is 1 mol

0.1000 g   is X mol.

$X = 7.46 \times 10^{-4}$ mol $Na_2C_2O_4$

According to the reaction above;

2 mol of $KMnO_4$ react with 5 mol of $C_2O_4^{2-}$, then

X mol of $KMnO_4$ react with 7.46×10^{-4} mol $C_2O_4^{2-}$.

$X = 2.98 \times 10^{-4}$ mol of $KMnO_4$ is required.

15.0 mL of $KMnO_4$ solution   have 2.98×10^{-4} mol of $KMnO_4$

1000 mL of $KMnO_4$ solution   have X mol of $KMnO_4$.

$X = 0.0198$ mol/L $KMnO_4 = 0.0198$ M $KMnO_4$

## 2.2.1.1. Determination of Nitrite Ion

Nitrite ion under acidic conditions transforms as follows:

$$3\ NO_2^- + 3H^+ \longrightarrow HNO_3 + 2\ NO + H_2O$$

In order to prevent its transformation, acid solution can be added to the titrant.

Transfer 5.0 mL of standard $KMnO_4$ solution to a conical flask, dilute it with 50 mL of distilled water and add 5.0 mL of 1.0 M H_2SO_4 solution. Fill the burette with nitrite sample and titrate the $KMnO_4$ solution with sample solution until the solution changes its color from purple to colorless. Repeat the titration at least three times and record the average of the sample volumes consumed.

$$2MnO_4^- + 5\ NO_2^- + 6\ H^+ \longrightarrow 2\ Mn^{2+} + 5\ NO_3^- + 3H_2O$$
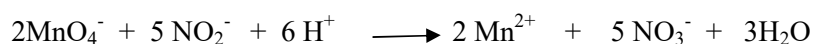
Calculations:

Calculate the amount of nitrite according to chemical reaction above.

Specimen results:

Average of the sample volumes consumed: 10.0 mL

$M_{KMnO4} = 0.0200$ M

$V_{KMnO4} = 5.0$ mL

$Mw_{NO2} = 46$ g/mol

While,

For 10 mL of nitrite sample   are required 5.0 mL of KMnO$_4$ solution

for 100 mL   X mL

X= 50 mL of KMnO$_4$ solution are required.

? m$_{NO2}$= 50 mL KMnO$_4$ **.** $\underline{\text{0.0200 mol KMnO}_4}$ **.** $\underline{\text{5 mol NO}_2^-}$ **.** $\underline{\text{46 g NO}_2^-}$

                                        1000 mL KMnO$_4$ 2 mol KMnO$_4$ 1 mol NO$_2^-$

m$_{NO2}$= 115 mg/100mL

II. Solution Route:

While,

1000 mL of KMnO$_4$ solution   have 0.0200 mol of KMnO$_4$,

$\underline{\text{50 mL of KMnO}_4 \text{ solution}}$ have X mol of KMnO$_4$.

 X= 1 x 10^{-3} mol KMnO$_4$

According to the reaction occured,

2 mol KMnO$_4$ react with 5 mol NO$_2^-$, then

$\underline{\text{1 x 10}^{-3} \text{ mol KMnO}_4}$ react with X mol NO$_2^-$.

X= 2.5 x 10^{-3} mol NO$_2^-$

1 mol NO$_2^-$ is 46 g

$\underline{\text{2.5 x 10}^{-3} \text{ mol NO}_2^-}$ is X g.

X= 0.115 g = 115 mg NO$_2^-$/100 mL

2.2.1.2. Determination of Manganese by Volhard's Volumetric Method

Volhard's volumetric method for manganese is based upon the following reaction which takes place in a hot neutral solution.

$$2 \ MnO_4^- + 3Mn^{2+} + 6 \ H_2O \longrightarrow 5 \ MnO_2 + 4 \ H_3O^+$$

ZnO, a water-immiscible base, is added for the purpose of providing a neutral solution, since it reacts hydronium ions. Zn^{2+} cation formed is also absorbed by MnO$_2$.

Pipette 25.0 mL of sample solution into a conical flask, dilute it with 50 mL of distilled water and add 1 spoon of ZnO. Heat the content of the flask up to 80-90 °C. Fill the burette with KMnO$_4$ solution and the titrant is slowly added to the sample solution until the solution

changes its color from colorless to purple. Repeat the titration at least three times and record the average of titrant volumes consumed.

Calculations:

Calculate the amount of manganese according to chemical reaction above.

Specimen results:

Average of the titrant volumes consumed (V_{KMnO4}): 5.0 mL

M_{KMnO4}= 0.0200 M

Mw_{Mn}= 55 g/mol

? m_{Mn2+}= 5.0 mL KMnO$_4$. $\dfrac{0.0200\ \text{mol KMnO}_4}{1000\ \text{mL KMnO}_4}$. $\dfrac{3\ \text{mol Mn}^{2+}}{\text{mol KMnO}_4}$. $\dfrac{55\ \text{g Mn}^{2+}}{1\ \text{mol Mn}^{2+}}$. $\dfrac{100\ \text{mL}}{25\ \text{mL}}$

?   = 33 mg Mn^{2+}/100 mL

II. Solution Route:

While,

1000 mL of KMnO$_4$ solution   have 0.0200 mol of KMnO$_4$,
5.0 mL of KMnO$_4$ solution   have X mol of KMnO$_4$.
 X= 1 x 10^{-4} mol KMnO$_4$

According to the reaction occured,

2 mol   MnO$_4^-$ react with 3 mol Mn^{2+} , then
1 x 10^{-4} mol MnO$_4^-$ react with X mol Mn^{2+}.
X= 1.5 x 10^{-4} mol Mn^{2+}

1 mol Mn^{2+} is 55 g   25 mL   contain 8.25 mg of Mn^{2+}, then
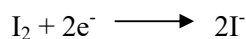1.5 x 10^{-4} mol Mn^{2+} is X g.   100 mL   contain X mg of Mn^{2+}.
X= 8.25 x 10^{-3} g Mn^{2+} = 8.25 mg Mn^{2+} X= 33 mg Mn^{2+} /100 mL

2.2.2. Iodometry

Iodine, which is an oxidizing agent, reduces itself to iodide while oxidizing others in its reactions.

$I_2 + 2e^- \longrightarrow 2I^-$

Titrations using adjusted iodine solution is called iodimetry, the titrations using quantitation of an oxidant performed by titration of iodine, which results from reaction of an oxidizing agent with iodide, with thiosulphate solution is called iodometry.

For quantitation of an oxidizing analyte in iodometric titrations, the medium is first acidified and then excess KI is added. In the presence of the oxidizing agent, iodide is oxidized to iodine. The emerging iodine reacts with excess iodide and forms highly soluble triiodide in water:

$$I_2 + I^- \longrightarrow I_3^-$$
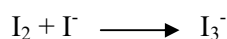
When the emerging triiodide/iodine is titrated with the adjusted thiosulfate solution,

$$I_3^- + 2S_2O_3^{2-} \longrightarrow 3I^- + S_4O_6^{2-}$$
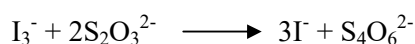
Iodine is reduced to iodide according to the reaction, while thiosulfate is oxidized to tetrathionate. The equivalent amount of thiosulfate solution consumed at the end of the titration is equal to the oxidizing analyte and the quantitation is carried out based on this equation.

Starch is used as an indicator in iodometric titrations. However, as the starch decays in the acidic medium, it should be added to the medium at the end of the titration. When red-brown color resulting from iodine turns into yellow during titration, the starch should be added to the medium and the titration with thiosulfate solution should be continued until the blue color is removed.

Preparation of 0.1 M Sodium Thiosulphate Solution

Weigh about 24.82 g $Na_2S_2O_3.5H_2O$ ($Na_2S_2O_3.5H_2O$; M_A=248.19 g/mol) into a conical flask, dissolve with distilled water, transfer to a 1.0 L volumetric flask and dilute to mark with distilled water and mix well.

Standardization of 0.1 M Na₂S₂O₃ Solution

$Na_2S_2O_3$ is not a primary standard and thus a freshly prepared solution of this chemical must be standardized. For this purpose, primary standards ($K_2Cr_2O_7$, KIO_3, $KBrO_3$ or pure copper wire) or standardized solutions as the secondary standard (standardized $KMnO_4$ or iodine solutions) can be used to determine the exact concentration of the $Na_2S_2O_3$ solution.

Weigh about 1 g of KI and transfer to a 250 mL conical flask. Dissolve in 50 mL of distilled water and add 2.0 mL of concentrated HCl solution. Mix well until the KI dissolves. Transfer 5.0 mL of standard $KMnO_4$ solution to the conical flask. Cover the flask with a watch glass and store in the dark for 10 min in order to complete the reaction.

Fill the burette with $Na_2S_2O_3$ solution prepared and after 10 min, titration is carried out until the single drop of $Na_2S_2O_3$ makes the solution colorless. Repeat the titration at least three times, find the average of titrant volumes and calculate the real molarity of the $Na_2S_2O_3$ solution. Record the value on the bottle lable.

Chemical reactions occured between $KMnO_4$ and KI and during titration may be represented as:

$$2\ MnO_4^- + 15\ I^- + 16\ H^+ \longrightarrow 2\ Mn^{2+} + 5\ I_3^- + 8H_2O$$

$$I_3^- + 2S_2O_3^{2-} \longrightarrow 3I^- + S_4O_6^{2-}$$

There is this equation at the end point:

$$M_{KMnO4}\ x\ V_{KMnO4} = M_{Na2S2O3}\ x\ V_{Na2S2O3}$$

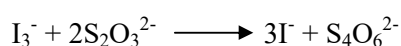## 2.2.2.1. Determination of Dichromate Ion

Transfer 10.0 mL of sample solution to a conical flask and dilute with distilled water about 50 mL. Add 1.0 mL of concentrated HCl solution and 1 spoon of KI. The flask is covered with watch glass and allowed to stand for 5 min to allow the reaction to complete in the dark. After 5 min, the solution will turn a dark-brown color and immediately titrate it with the standardized thiosulfate solution. When the color of the solution becomes very pale yellow add 1 mL of starch indicator. Continue the titration until the blue color of the starch complex just disappears. Repeat the titration at least three times and find the average of titrant volumes.

Calculations

Chemical reaction occured between dichromate ion and iodide;

$$Cr_2O_7^{2-} + 16\ H^+ + 9I^- \longrightarrow 2Cr^{3+} + 3I_3^- + 7H_2O$$
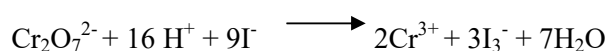
The following reaction takes place during titration;

$$I_3^- + 2S_2O_3^{2-} \longrightarrow 3I^- + S_4O_6^{2-}$$

Calculate the amount of dichromate ion according to chemical reaction above.

Specimen results:

Average of the titrant volumes consumed ($V_{Na2S2O3}$): 10.0 mL

$M_{Na2S2O3}$= 0.1000 M

Mw_{Cr2O7}= 216 g/mol

? m $Cr_2O_7^{2-}$= 10.0 mL $Na_2S_2O_3$. $\underline{0.1000\ mol\ Na_2S_2O_3}$.$\underline{1\ mol\ Cr_2O_7^{2-}}$. $\underline{216\ g\ Cr_2O_7^{2-}}$ .10

$\qquad\qquad\qquad\qquad$ 1000 mL $Na_2S_2O_3$ $\quad$ 6 mol $Na_2S_2O_3$ $\ $ 1 mol $Cr_2O_7^{2-}$

? = 360 mg $Cr_2O_7^{2-}$/100 mL

II. Solution Route:

While,

1000 mL of $Na_2S_2O_3$ solution $\qquad$ have 0.1000 mol of $Na_2S_2O_3$
$\underline{10.0\ mL\ of\ Na_2S_2O_3\ solution}$ $\qquad$ have X mol.
X= 1 x 10^{-3} mol $Na_2S_2O_3$

6 mol $S_2O_3^{2-}$ $\qquad\qquad$ react with 1 mol $Cr_2O_7^{2-}$, then
$\underline{1\ x\ 10^{-3}\ mol\ S_2O_3^{2-}}$ $\qquad$ react with X mol $Cr_2O_7^{2-}$.
X= 1.667 x 10^{-4} mol $Cr_2O_7^{2-}$

1 mol $Cr_2O_7^{2-}$ $\qquad\qquad$ is 216 g $\qquad$ If 10 mL of sample $\quad$ contain 36 mg $Cr_2O_7^{2-}$,
$\underline{1.667\ x\ 10^{-4}\ mol\ Cr_2O_7^{2-}}$ $\qquad$ is X g. $\qquad$ $\underline{100\ mL\ of\ sample}$ $\qquad$ contain X mg $Cr_2O_7^{2-}$.
X= 3.6 x 10^{-2} g $Cr_2O_7^{2-}$ = 36 mg $Cr_2O_7^{2-}$ $\qquad$ X= 360 mg $Cr_2O_7^{2-}$/100 mL

2.2.2.2. Determination of Active Chlorine in Hypochlorite Solution

Chlorine (Cl_2) is a gas, toxic, non-flammable and an economically available oxidizing agent that provides properties desirable in disinfection usage. Chlorine is available in one of three forms: sodium hypochlorite, calcium hypochlorite and liquid chlorine. Sodium hypochlorite, commonly called "liquid bleach", is commercially available in strengths approximately 15% by weight. Calcium hypochlorite, generally referred to as "powder chlorine". It contains 70% available chlorine. Liquid chlorine, known also as "chlorine gas", is chlorine in its elemental form. When comparing elemental chlorine as an oxidizing agent to powder (calcium hypochlorite) or solution (sodium hypochlorite), the oxidizing effect is the same. All of them oxide iodide to I_2 in acidic media.

$$OCl^- + Cl^- + H^+ \longrightarrow Cl_2 + H_2O$$

$$Cl_2 + 3I^- \longrightarrow 2Cl^- + I_3^-$$

$$OCl^- + 3I^- + 2H^+ \longrightarrow Cl^- + I_3^- + H_2O$$
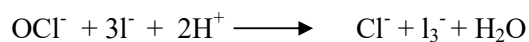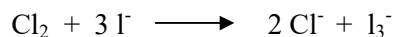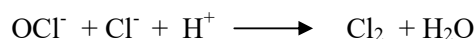
The thiosulfate ion reacts with I_3 producing iodide ions:
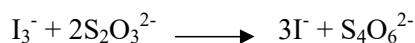
$$I_3^- + 2S_2O_3^{2-} \longrightarrow 3I^- + S_4O_6^{2-}$$

Take your sample which is provided in a 100 mL volumetric flask and add distilled water till the its mark. Shake the solution well and transfer 25.0 mL of sample with pipette into a conical flask. Add 1.0 mL of 0.1 M HCl solution and 1 spoon of KI. The flask is covered with watch glass and store in the dark for 5-10 min.

Titrate with standardized $Na_2S_2O_3$ solution until the color of the sample solution disappears. Repeat the titration at least three times and find the average of titrant volumes.

Calculations:

Specimen results:

Average of the titrant volumes consumed ($V_{Na2S2O3}$): 10.0 mL

$M_{Na2S2O3}$= 0.1000 M

Mw_{Cl2}= 71 g/mol

? m Cl₂= 10.0 mL Na₂S₂O₃. $\underline{\text{0.1000 mol Na}_2\text{S}_2\text{O}_3}$.$\underline{\text{1 mol Cl}^-}$. $\underline{\text{71 g Cl}_2}$. $\underline{\text{100 mL}}$

1000 mL Na₂S₂O₃   2 mol Na₂S₂O₃ 1 mol Cl₂ 25 mL

? = 142 mg Cl₂/100 mL

II. Solution Route:

While,

1000 mL of $Na_2S_2O_3$ solution   have 0.1000 mol of $Na_2S_2O_3$

<u>10.0 mL $Na_2S_2O_3$ solution</u>   have X mol.

$X = 1 \times 10^{-3}$ mol $Na_2S_2O_3$

If 2 mol $S_2O_3^{2-}$ react with 1 mol Cl^-,

<u>1×10^{-3} mol $S_2O_3^{2-}$</u>   react with X mol Cl^-.

$X = 5 \times 10^{-4}$ mol Cl^-

| 1 mol Cl_2 is 71 g	If 25 mL contain 35.5 mg Cl_2,
5×10^{-4} mol Cl_2 is X g.	100 mL contain X mg Cl_2.
X= $3,55 \times 10^{-2}$ g Cl_2 = 35,5 mg Cl_2	X= 142 mg Cl_2 /100 mL

2.2.3. Bromometry

The relatively high standard oxidation strength of a redox couple BrO_3^-/Br^- system (E^0 = +1,44 V) indicates that potassium bromate is a strong oxidizing agent. The bromate is quantitatively reduced to bromine in the direct titration of the reducing agents in sufficient strength with potassium bromate in an acidic medium and the following reaction takes place:

$$BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$$

As (III), Sb (III), Sn (II), Tl (I), Fe $(CN)_6^{4-}$, hydrazine and many other reducing agents can be directly titrated with the bromate solution and they are determined. Direct titrations with $KBrO_3$ are performed in the presence of indicators such as methyl orange, methyl reds, etc.

Many substances are not directly oxidized with potassium bromate, but react quantitatively with excess elemental bromine. For this purpose, the system is first acidified to form free bromine in the known amount and the excess amount of KBr is added to the medium. Subsequently, a certain amount of $KBrO_3$ in the form of solid or standard solution is added to the medium and elemental bromine is formed in known quantities.

$$BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$
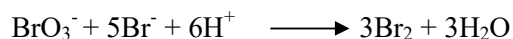
Without reaction, the excess bromine is reacted with excess KI and the iodine released is titrated with the thiosulfate solution.

$$Br_2 + 2I^- \longrightarrow I_2 + 2Br^-$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$
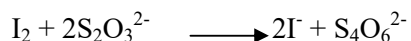
Since the consumed thiosulfate solution corresponds to the excess of the standard bromate solution, the difference between the initial solution of bromate and its excess is used to calculate the amount of the analyte. Quantitative determination of many metal ions and some organic compounds such as phenols and aniline can be carried out indirectly by means of potassium bromate solution.

Preparation of 0.02 M Potassium Bromate Solution

Dry potassium bromate at 120 ^{0}C at least 1 h and cool in a desiccator. Weigh about 3.34 g KBrO$_3$ (M$_A$: 167 g/mol) into a 1 L volumetric flask. Dilute to the mark with distilled water and mix thoroughly.

Standardization of 0.02 M KBrO$_3$ Solution

Transfer 10.0 mL of KBrO$_3$ solution prepared to the conical flask, add 2.0 mL of concentrated HCl solution and 1 spoon of solid KI. Cover the flask with a watch glass and store in the dark for 10 min in order to complete the reaction. Fill the burette with standardized Na$_2$S$_2$O$_3$ solution and after 10 min, titration is carried out until the single drop of Na$_2$S$_2$O$_3$ makes the solution colorless. Repeat the titration at least three times and find the average of titrant volumes.

Chemical reactions occured between BrO$_3^-$ and I$^-$ and during titration as follows:

$$BrO_3^- + 6I^- + 6H^+ \longrightarrow 3I_2 + Br^- + 3H_2O$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$
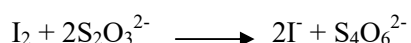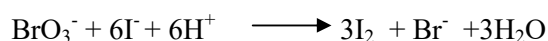
Calculate the real molarity of the KBrO$_3$ solution.

M$_{Na2S2O3}$ x V$_{Na2S2O3}$ = M$_{KBrO3}$ x V$_{KBrO3}$

2.2.3.1. Determination of Arsenic(III)

Pipette 25.0 mL of sample solution into a conical flask, dilute it with 50-75 mL of distilled water and add 15.0 mL of concentrated HCl solution. Add 2-3 drops of methyl orange indicator (red color) and titrate slowly the sample with standard KBrO$_3$ solution till the indicator turns colorless. Repeat the titration at least three times and record the average of titrant volumes consumed.

Calculations:

$$BrO_3^- + 3As^{3+} + 9H_2O \longrightarrow H_3AsO_4 + Br^- + 9H^+$$
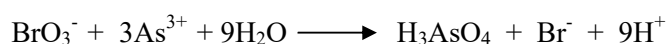
Specimen results:

Average of the titrant volumes consumed (V$_{KBrO3}$): 10.0 mL

M$_{KBrO3}$= 0.0200 M

Mw $_{As3+}$= 75 g/mol

? m As^{3+} = 10.0 mL KBrO$_3$. $\underline{0.0200 \text{ mol KBrO}_3}$. $\underline{3 \text{ mol As}^{3+}}$. $\underline{75 \text{ g As}^{3+}}$. $\underline{100 \text{ mL}}$

 1000 mL KBrO$_3$ 1 mol KBrO$_3$ 1 mol As^{3+} 25 mL

? = 180 mg As^{3+}/100 mL

II. Solution Route:

While,

1000 mL of KBrO$_3$ solution have 0.0200 mol of KBrO$_3$

$\underline{\text{10.0 mL KBrO}_3 \text{ solution}}$ $\underline{\text{have X mol.}}$

X= 2 x 10^{-4} mol KBrO$_3$

1 mol BrO$_3^-$ react with 3 mol As^{3+} ,

$\underline{2 \text{ x } 10^{-4} \text{ mol BrO}_3^-}$ $\underline{\text{react with X mol As}^{3+}}$.

X= 6 x 10^{-4} mol As^{3+}

1 mol As^{3+} is 75 g If 25 mL contain 45 mg of As^{3+} ,

$\underline{6 \text{ x } 10^{-4} \text{ mol As}^{3+}}$ $\underline{\text{is X g.}}$ $\underline{\text{100 mL}}$ $\underline{\text{contain X mg As}^{3+}}$.

X= 4.5 x 10^{-2} g As^{3+} = 45 mg As^{3+} X= 180 mg As^{3+}/100 mL

2.2.4. Dichromate Titrations

The dichromate solution is not used as widely as the permanganate solution. However, due to the fact that the solution is very durable, it is more preferred than the permanganate especially in the titrations performed in the hot. Dichromate solution is prepared from potassium dichromate. The ability of potassium dichromate to be sufficiently pure or to be purified by recrystallization is another superiority over potassium permanganate. Dissolution of 96.2 grams at 90 ˚C and 13.1 grams at 20 ˚C in 100 mL of water allows the easy crystallization of potassium dichromate. In the neutral medium, the fact that dichromate does not react easily with organic substances in the cold and it is not affected by light, is the other superior aspects of dichromate over permanganate. The dichromate solution can be used for direct titration of all the reducing agents allowed by the standard potential. It is also used with Fe (II) solution in the back titration of some oxidants.

Preparation of 0.02 M Potassium Dichromate Solution

Dry $K_2Cr_2O_7$ for at least 30-60 min at 140-150 ^0C and cool in a desiccator. Weigh out 4.9032 g $K_2Cr_2O_7$ (M_A: 294 g/mol) into a 1 L volumetric flask. Dilute to the mark with distilled water and mix well.

Standardization of 0.02 M $K_2Cr_2O_7$ Solution

Weigh out 0.2 g of $(NH_4)_2Fe(SO_4)_2.6H_2O$ into a conical flask and add 50 mL of distilled water to dissolve the salt. Acidify with 5.0 mL of concentrated H_3PO_4 solution and add 0,5 mL of diphenylamine sulfonate indicator. Titrate slowly with $K_2Cr_2O_7$ solution to the violet-blue end point and record the volume of titrant.

$$6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^+ \longrightarrow 6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$$

Calculations:

If 392 g of $(NH_4)_2Fe(SO_4)_2.6H_2O$ contain 56 g of Fe^{2+} ,

0,2 g of compound   contain X g of Fe^{2+}

X = 0,028 g Fe^{2+}

Specimen results:

m_{Fe2+}=0.028 g

$V_{K2Cr2O7}$ = 4.0 mL

Mw_{Fe}= 56 g/mol

0.028 g Fe = 4.0 mL $K_2Cr_2O_7$. **X mol $K_2Cr_2O_7$** .   6 mol Fe   .   56 g Fe

                                     1000 mL $K_2Cr_2O_7$ 1 mol $K_2Cr_2O_7$ 1 mol Fe

X= 0.0208 M $K_2Cr_2O_7$

II. Solution Route:

While,

56 g   Fe   is 1 mol,

0.028 g Fe   is X mol.

X= 5 x 10^{-4} mol Fe

According to the chemical reaction above;

1 mol of $Cr_2O_7^{2-}$ react with 6 mol of Fe^{2+} , then

X mol of $Cr_2O_7^{2-}$ react with 5 x 10^{-4} mol Fe^{2+}.

X= 8.33 x 10^{-5} mol of $K_2Cr_2O_7$ are required.

If 4.0 mL of $K_2Cr_2O_7$ solution   contain 8.33 x 10^{-5} mol of $K_2Cr_2O_7$,

<u>1000 mL of $K_2Cr_2O_7$ solution</u>   contain X mol of $K_2Cr_2O_7$.

X= 0.0208 mol/L $K_2Cr_2O_7$

2.2.4.1. Determination of Iron(II)-Iron(III)

Transfer 25.0 mL of sample solution with a pipette to a conical flask and dilute with distilled water about 100 mL. Add 2.0 mL of concentrated H_2SO_4 solution and 1.0 mL of concentrated H_3PO_4 solution and diphenylamine sulfonate indicator. After cooling, iron(II) ions in the sample is titrated with standard $K_2Cr_2O_7$ solution and note the volume of titrant (V_1). Take the second sample having the same volume and reduce with a proper reducing agent.

<u>Carry out one of the methods below for the reduction process</u>

1- *Reduction with SnCl$_2$:*

Add 3.0 mL of concentrated H_2SO_4 to the sample solution and heat the content of the sample up to 70-90 °C. Add concentrated $SnCl_2$ solution dropwise until the yellow color disappears. At the end of the reduction of iron(III), the solution remains pale green in stead of yellow color

$$2\ Fe^{3+} + Sn^{2+} \longleftrightarrow 2\ Fe^{2+} + Sn^{4+}$$
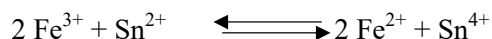
Cool to room temperature and add 10 mL of $HgCl_2$ (5%, w/w). A small of quantity of a white precipitate of Hg_2Cl_2 should appear (color of the precipitate should not be gray). After reduction process, Add 2.0 mL of concentrated H_2SO_4 and 1.0 mL of concentrated H_3PO_4, cool, and add 0.5 mL of diphenylamine sulfonate indicator. The total iron in the sample is titrate with standard $K_2Cr_2O_7$ solution and note the volume of titrant (V_2).

2- *Reduction with Amalgamated Zinc (The Jones reductor)*

Weigh about 300 g of zinc powder into a conical flask and $HgCl_2$ solution is added in excess to cover it. The zinc is amalgamated by mixing about 5-10 min. To prevent the formation of basic salt by oxidizing, keep in water the grain of zinc amalgamated. Take a 25 mL burette covered with a little glass wool at the bottom, fill it with zinc amalgamated and water. Rinse the burette with 50 mL of 1.0 M H_2SO_4. For reduction process, transfer a 100 mL aliquot of the sample solution acidifying 5.5 mL of concentrated H_2SO_4 into the burette and adjust the

flow rate of the sample solution as 75 mL/min at least. After the passing of the sample solution, rinse the burette with 50 mL of 1.0 M H_2SO_4 and 50-75 mL of distilled water. When not in use the reductor should be kept filled with water to prevent oxidation.

Calculations:

Chemical reaction occured between iron(II) and dichromate ion:

$$6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^+ \longrightarrow 6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$$
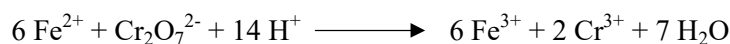
The titrant volume consumed in the first titration is used for the calculation of the amnount of iron(II).

$$V_1 = V_{Fe2+}$$

After reduction with $SnCl_2$, the titrant volume consumed in the second titration equals to the total volume required for iron(II) and iron(III)

$$V_2 = V_{Total(Fe2+ + Fe3+)}$$

the titrant volume required for iron(III):

$$V_{Fe3+} = V_2 - V_1$$

Specimen Results:

$M_{K2Cr2O7}$=0.0200 M

$V_1 = 5.0$ mL

$V_2 = 12.0$ mL

$V_{Fe2+} = 5.0$ mL

$V_{Fe3+} = 12.0-5.0 = 7.0$ mL

?mFe^{2+} = 5.0 mL $K_2Cr_2O_7$. $\dfrac{0.0200\ mol\ K_2Cr_2O_7}{1000\ mL\ K_2Cr_2O_7}$. $\dfrac{6\ mol\ Fe^{2+}}{1\ mol\ K_2Cr_2O_7}$. $\dfrac{56\ g\ Fe^{2+}}{1\ mol\ Fe^{2+}}$. $\dfrac{100\ mL}{25\ mL}$

?$_{Fe2+}$ = 134.4 mg Fe^{2+}/100 mL

?$_{Fe3+}$ = 188.2 mg Fe^{3+}/100 mL

II. Solution Route:

While,

1000 mL of $K_2Cr_2O_7$ solution   have 0.0200 mol of $K_2Cr_2O_7$

5.0 mL $K_2Cr_2O_7$ solution   have X mol.

X= 1 x 10^{-4} mol $K_2Cr_2O_7$

1 mol $Cr_2O_7^{2-}$ react with 6 mol Fe^{2+}, then

$\underline{1 \times 10^{-4} \text{ mol } Cr_2O_7^{2-}}$ react with X mol Fe^{2+}.

$X = 6 \times 10^{-4}$ mol Fe^{2+}

1 mol Fe^{2+}	is 56 g,	If 25 mL	contain 33.6 mg Fe^{2+},
$\underline{6 \times 10^{-4} \text{ mol } Fe^{2+}}$	is X g.	$\underline{100 \text{ mL}}$	contain X mg Fe^{2+}.
$X = 3.36 \times 10^{-2}$ g $Fe^{2+} = 33.6$ mg Fe^{2+}		$X = 134.4$ mg $Fe^{2+}/100$ mL	

The amount of Fe(III) is similarly calculated by 7.0 mL.

## 2.3. Precipitation Titrations

Precipitation titrations result in compounds with limited solubility during titration. The zinc, sulphate, molybdate phosphate, oxalate, mercury (I) ions can be quantitatively determined using potassium ferrocyanide, lead nitrate, lead acetate, barium chloride, sodium chloride solutions as titrant. However, when it is said precipitation titrations the first thing that comes to mind is the usage of more silver nitrate and determinations of chlorine, bromide and iodide. These titrations, in which silver ions are used, are also called Argentometry. Argentometric titrations are divided into three groups as Mohr, Volhard and Fajans methods.

Preparation of 0.1 M Siver Nitrate Solution

Dry about 20 g of $AgNO_3$ at 120 ˚C for at least 2 h and cool in a desiccator. Weigh 17 g of the salt into a conical flask, dissolve with distilled water, transfer to a 1 L volumetric flask and dilute to the mark with distilled water and mix thoroughly.

Standardization of the AgNO$_3$ Solution

Dry pure NaCl for 1- 2 h at 250-350 ˚C and cool in a desiccator. Weigh 2.923 g into a volumetric flask and dissolve in 500 mL of distilled water. Molar concentration of this solution is 0.1 M. Pipette 25.0 mL of the solution into a conical flask, dilute it with 50-75 mL of distilled water and add 10 drops of fluorescein. Titrate with $AgNO_3$ solution prepared until the precipitate turns pink. Repeat the titration at least three times and record the average of titrant volumes consumed.

$Ag^+ + Cl^- \longrightarrow AgCl$
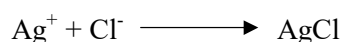
Calculations:

2.923/20= 0.1461 g NaCl=V mL $AgNO_3$. **X mol $AgNO_3$** . 58.44 g NaCl = ...M $AgNO_3$

1000 mL $AgNO_3$ 1 mol NaCl

2.3.1. Determination of Bromide Ion

Pipette acuurately 25.0 mL of the sample solution into a conical flask and dilute it to 75-100 mL with distilled water. Add 2-3 mL 6.0 M CH_3COOH and 10 drops of eosine indicator. Titrate with standardized $AgNO_3$ solution to the end point where the color of the precipitate just changes to pink.

Calculations:

Chemical reaction occured during titration:

$Ag^+ + Br^- \longrightarrow AgBr$
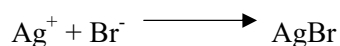
Specimen results:

M_{AgNO3}=0.1000 M

V_{AgNO3} = 10.0 mL

Mw_{Br}= 80 g/mol

? m Br^- =10.0 mL $AgNO_3$. 0.1000 mol $AgNO_3$. 1 mol Br^- . 80 g Br^- . 100 mL

1000 mL $AgNO_3$ 1 mol $AgNO_3$ 1 mol Br^- 25 mL

?   = 320 mg Br^-/100 mL

II. Solution Route:

While,

1000 mL of $AgNO_3$ solution   have 0.1000 mol of $AgNO_3$

10.0 mL of $AgNO_3$ solution   have X mol.

X= 1 x 10^{-3} mol $AgNO_3$

At the end of the titration, the mole number of $AgNO_3$ equals to the mole number of bromide.

1 mol Br^-	is 80 g,		If 25 mL	contain 80 mg of Br^-,
1 x 10^{-3} mol Br^-	is X g.		100 mL	contain X of mg Br^-.

X= 8.0 x 10^{-2} g Br^- = 80 mg Br^- X= 320 mg Br^-/100 mL

2.4. Complexometry

The new structure formed by one or more central atoms and charged or uncharged ion called the ligands attached to them or ion groups or molecules, is called **complex.** If the central atom is one, it is called a mononuclear complex, and if the central atom is a few, it is called polynuclear complexes. Central atom functions as electron acceptor (acceptor), ligand functions as electron donor (donor).

The number of groups attached to the central atom is called the number of ligands (= number of coordination). A central atom can usually accept ligands twice its charge. For example, as Ag has valence of +1 in $Ag(NH_3)_2^+$ it can accept maximum two ligands and as Cu has valence of +2 it can accept maximum four ligands.
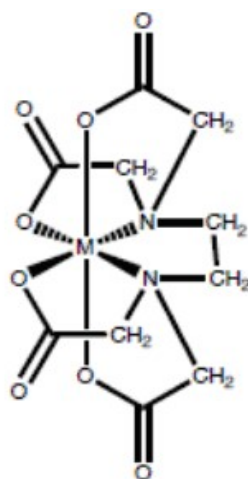
If a compound contains more than one group that is an electron donor, several groups of the same molecule coordinate with the same metal ion. Complexes formed by the coordination of several groups on the same ligand with the same metal ion are thus called **chelate complexes**.

EDTA Titrations

Ethylene Diamine Tetra Acetic Acid (EDTA) is the most commonly used as chelating agent in practical applications. EDTA forms 1: 1 complexes with +2 and +3 valence ions. EDTA forms the chelate complexes to be hexadentate with metals using six unduplicated electron pairs, two on nitrogen atoms and four on oxygen in the carboxyl groups.
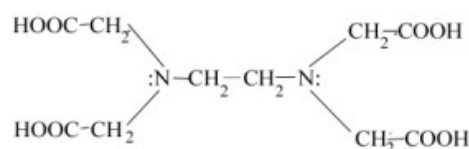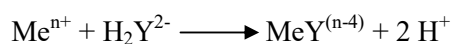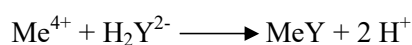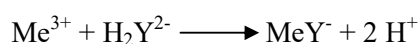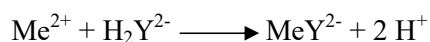

Etilen Diamin Tetra Asetikasit (EDTA)   Metal-EDTA şelatı

EDTA is insoluble in water. To dissolve in water, the compound containing the disodium salt should be used. On the market, these are sold in titles such as Komplekson® III, Titriplex® III.

EDTA is shown as (HY_4) and disodium salt is shown as $(Na_2H_2Y.2H_2O)$. The ions in aqueous solution are also shown as H_2Y^{2-}. The reaction of this ion with metal ions of different valence is as given below.

$Me^{2+} + H_2Y^{2-} \longrightarrow MeY^{2-} + 2\ H^+$

$Me^{3+} + H_2Y^{2-} \longrightarrow MeY^- + 2\ H^+$

$Me^{4+} + H_2Y^{2-} \longrightarrow MeY + 2\ H^+$

$Me^{n+} + H_2Y^{2-} \longrightarrow MeY^{(n-4)} + 2\ H^+$

As can be seen in the equations, Me-Ligand ratio is 1 in EDTA complexes with metal ions.

EDTA titrations are usually performed in two ways.

1- Direct Titration:

In this method, the aqueous solution of metal salts is titrated with a sodium EDTA solution adjusted with the aid of a metallic indicator. For this reaction to occur thoroughly, titration is carried out in basic medium and by usually using ammonia buffer solutions with a pH of 10. This method can be applied to the determination of cations, which do not precipitate as hydroxides at pH = 10 and form stable chelate compounds with EDTA; For example; Mg, Ca, Sr, Ba, rare earth elements (Lanthanides), metals such as Th, Fe (III), Co, Cu, Pb and Bi can be determined by EDTA. Another requirement for cations to be titrated with this method is the presence of a suitable indicator.

2- Indirect Titration:

Some metals cannot be directly titrated since they precipitate in the form of hydroxides at pH 10 with EDTA. In this regard, the metal is treated with an excess of EDTA at low pH at a sufficient level. The solution is then buffered and it is adjusted to a high pH. The excess of EDTA is titrated using the appropriate indicator with adjusted Zn^{2+} or Mg^{2+}. Since the metal to be titrated in this determination is first complexed with EDTA, it does not precipitates when pH rises and it has no effect on the indicator reaction. This method is used in the determination of Co, Ni, Cu, Al, Fe, Ti and some other metals.

Buffer solutions: Since formation and stability of metal complexes depend on pH, most complexometric titration should be performed in buffered medium. For this purpose, pH 10 buffer is usually used.

__Preparation of ammonia-ammonium chloride solution (pH: 10 buffer):__ After 54 g of ammonium chloride is dissolved in approximately 200 mL of destilled water, 350 mL of concentrated ammonia solution (25%, d: 0.91 g / mL) is added and it is completed up to 1.0 L with distilled water in a volumetric flask. This buffer solution is suitable for all titrations, in which Erio T is used as an indicator.

The substances used as indicators in EDTA titrations are ligands that form complex with the metal ion in general. These substances are called metal indicators or monochromatic indicators. The indicator-metal complex of these indicators should be less stable than EDTA-metal complex. Erio-T, xylene orange, pyrocatechol violet, PAN, PAR, ditizone and murexite are the most commonly used indicators in these titrations.

__Preparation of 0.1 M EDTA Solution__

Dry $Na_2H_2C_{10}H_{12}O_2N_2.2H_2O$ at 80 ˚C for at least 1 h and cool in a desiccator. Weigh 37.225 g of the salt into a conical flask, dissolve with distilled water, transfer to a 1.0 L volumetric flask and dilute to the mark with distilled water. Mix well by inverting and shaking the tightly stoppered flask. Label this solution "Standard EDTA" and calculate its real molarity.

__Standardization of 0.1 M EDTA Solution__

Transfer 1.0 mL of Fe^{3+} solution (C_{Fe}=14 mg/mL) into a conical flask and dilute it with 50 mL of distilled water. Control pH of the solution; it should be 2.5 (if not, adjust with diluted NH_4OH or HCl). Add 0.5 mL of 5-sulfosalicylic acid indicator and titrate with EDTA solution prepared until the indicator turns from red to colorless.

__Calculations:__

Specimen results:

m_{Fe3+}= 14 mg

V_{EDTA}= 2.6 mL

0.014 g Fe = 2.6 mL EDTA . $\underline{\textbf{X} \text{ mol EDTA}}$. $\underline{\text{1 mol Fe}}$. $\underline{\text{56 g Fe}}$
                                                1000 mL EDTA   1 mol EDTA   1 mol Fe

X= 0.0961 M

II. Solution Route:

While,

56 g   Fe   is 1 mol

0.014 g Fe   is X mol.

$X = 2.5 \times 10^{-4}$ mol Fe

At the end of the titration, the mole number of EDTA is 2.5×10^{-4}.

If 2.6 mL of EDTA solution   contain 2.5×10^{-4} mol of EDTA

1000 mL of EDTA solution   contain X mol of EDTA.

X= 0.0961 mol/L EDTA

2.4.1. Determination of Magnesium-Zinc

Transfer 20.0 mL of the sample solution into a conical flask and dilute it with 100 mL of distilled water. Add 2-3 mL of pH 10 buffer solution and 2-3 drops of Erio-T indicator. Titrate with standardized EDTA solution until the indicator turns from red to blue. Note the total volume of titrant required (V_1) for magnesium and zinc. Take the second sample having the same volume and add 3 spoon of NH_4F as a masking agent. Dilute it to 100 mL with distilled water, add 2-3 mL of pH 10 buffer solution and 2-3 drops of Erio-T indicator. Titrate with standardized EDTA solution until the indicator turns from red to blue. Note the volume of titrant required (V_2) for only zinc.

Masking agent: EDTA is a widely applicable complexing agent as it will complex with almost any metal. This can be a problem if selectivity is desired however. Selectivity can be controlled through pH. A second method for adding selectivity is to add a competing reagent called a masking agent. A masking reagent reacts with one of the species and allows titration of the second. This can be applied to a simple binary mixture or to a more complex mixture. Floride, cyanide, hydroxide, sulfosalicylic acid, tartarate, citrate, ammonium and iodide can be used as a masking agent.

Calculations:

Specimen results:

$M_{EDTA} = 0.1000$ M, $V_1 = 10.0$ mL, $V_2 = 4.0$ mL

$V_2 = V_{Zn} = 4.0$ mL ,

$V_1 - V_2 = V_{Mg} = 10.0 - 4.0 = 6.0$ mL.

? m Zn $^{2+}$= 4.0 mL EDTA . $\underline{0.1000 \text{ mol EDTA}}$. $\underline{1 \text{ mol Zn}^{2+}}$. $\underline{65 \text{ g Zn}^{2+}}$. $\underline{100 \text{ mL}}$

　　　　　　　　　　1000 mL EDTA　　　1 mol EDTA　1 mol Zn $^{2+}$　20 mL

?　　= 130 mg Zn $^{2+}$/100 mL

? m Mg $^{2+}$= 6.0 mL EDTA . $\underline{0.1000 \text{ mol EDTA}}$. $\underline{1 \text{ mol Mg}^{2+}}$. $\underline{24 \text{ g Mg}^{2+}}$. $\underline{100 \text{ mL}}$

　　　　　　　　　　1000 mL EDTA　　　1 mol EDTA　1 mol Mg $^{2+}$　20 mL

?　　= 72 mg Mg $^{2+}$/100 mL

II. Solution Route:

1000 mL of EDTA solution　　　have 0.1000 mol of EDTA

$\underline{4.0 \text{ mL EDTA}}$_solution　　　have X mol .

X= 4 x 10^{-4} mol EDTA

At the end of the titration, the mole number of Zn^{2+} is 4 x 10^{-4}.

1 mol Zn^{2+}　　　　　　　　is 65　g　　　　　If 20 mL　　　contain 26 mg of Zn $^{2+}$,

$\underline{4 \text{ x } 10^{-4} \text{ mol Zn}^{2+}}$_　　　　is X g.　　　　$\underline{100 \text{ mL}}$　　　contain　X mg Zn $^{2+}$.

X= 2.6 x 10^{-2} g Zn $^{2+}$= 26 mg Zn $^{2+}$　　X= 130 mg Zn $^{2+}$/100 mL

1000 mL of EDTA solution　　　have 0.1000 mol of EDTA

$\underline{6.0 \text{ mL EDTA}}$_çözeltisinde　　　have X mol.

X= 6 x 10^{-4} mol EDTA

At the end of the titration, the mole number of Mg $^{2+}$ is 6 x 10^{-4}.

1 mol Mg^{2+}　　　　　　　is 24　g　　　　　If 20 mL　　　contain 14.4 mg of Mg^{2+}

$\underline{6 \text{ x } 10^{-4} \text{ mol Mg}^{2+}}$_　　　　is X g.　　　　$\underline{100 \text{ mL}}$　　　contain X mg Mg^{2+}.

X= 1.44 x 10^{-2} g Mg $^{2+}$= 14.4 mg Mg $^{2+}$　　X= 72 mg Mg^{2+}/100 mL

2.4.2. Determination of Iron-Aluminum

Preparation of 0.1 M Zinc Sulfate Solution

Weigh 28.754 g of $ZnSO_4.7H_2O$ into a conical flask, dissolve with distilled water, transfer to a 1 L volumetric flask and dilute to the mark with distilled water

Standardization of ZnSO₄ Solution

Transfer 10.0 mL of $ZnSO_4$ solution prepared to a conical flask, dilute to 100 mL with distilled water, add 2.0 mL of pH 10 buffer solution and 2-3 drops of Erio-T indicator. Titrate with standardized EDTA solution until the indicator turns from red to blue.

There is this equation at the end point:

M_{ZnSO4} x V_{ZnSO4} = M_{EDTA} x V_{EDTA}

Titration of the Sample Solution:

Transfer 20.0 mL of the sample solution into a conical flask, dilute it with 100 mL of distilled water and adjust pH to 2-2.5. Add 0.5 mL of 5-sulfosalicylic acid indicator and titrate with standardized EDTA solution until the indicator turns from red to colorless. This volume of titrant is used for only iron in this pH. At the equivalence point, add 20.0 mL of standardized EDTA solution to the flask and boil it for two min. Suspend it in a water bath for 10 min. After cooling, adjust pH to 5-6 with diluted sodium acetate solution and add 2-3 drops of xylene orange indicator. Titrate with standardized $ZnSO_4$ solution until the indicator turns from yellow to red and determine the excess of EDTA solution by:

M_{ZnSO4} x V_{ZnSO4} = M_{EDTA} x V_{EDTA}

V_{EDTA} is the excess volume of EDTA solution. The volume of titrant required for aluminum is 20 - V_{EDTA}. Calculate the amounts of analytes as described above.

2.4.3. Determination of Sulfate Ion

$SO_4^{2-} + Ba^{2+} \rightarrow BaSO_4(k)$
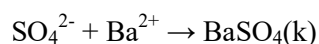
Take 10.0 mL of the sample solution into a conical flask and add 2-3 mL of 2.0 M HCl solution. Heat 5% $BaCl_2$ solution and add 15 mL of this solution to the flask. Suspend it in a water bath for 10 min for digestion. Filter the precipitation with blue filter paper, wash with distilled water in order to remove impurities and transfer the filter paper with precipitate to a beaker. Add 25.0 mL of standardized EDTA solution, 5.0 mL of concentrated NH_4OH and boil it for 10 min. Cool, add 3.0 mL of pH 10 buffer solution and 2-3 drops of Erio-T indicator. Titrate with standardized $MgCl_2$ solution until the indicator turns from blue to red.

M_{MgCl2} x V_{MgCl2} = M_{EDTA} x V_{EDTA}

V_{EDTA} is the excess volume of EDTA solution. The volume of titrant required for sulfate is: 25 - V_{EDTA}.

Calculations:

Specimen results:

M_{EDTA}= 0.0980 M

$V_{EDTA-added}$= 25.0 mL

M_{MgCl2}= 0.1000 M

V_{MgCl2}= 12.0 mL

M_{MgCl2} x V_{MgCl2} = M_{EDTA} x V_{EDTA}

0.1000 . 12.0 = 0.0980. V_{EDTA}

V_{EDTA} = 12.24 mL

25.0 – 12.24 = 12.76 mL of EDTA is required for the sulfate sample.

? m SO_4^{2-}= 12.76 mL EDTA . $\underline{0.0980\ mol\ EDTA}$. $\underline{1\ mol\ SO_4^{2-}}$. $\underline{96\ g\ SO_4^{2-}}$. $\underline{100\ mL}$

$\quad\quad\quad\quad\quad\quad\quad\quad$ 1000 mL EDTA $\quad\quad$ 1 mol EDTA $\quad$ 1 mol SO_4^{2-} $\quad$ 10 mL

? = 1200 mg SO_4^{2-}/100 mL

II. Solution Route:

1000 mL of EDTA solution $\quad\quad\quad$ have 0.0980 mol of EDTA

$\underline{12.76*\ mL\ of\ EDTA\ solution}$ $\quad\quad$ $\underline{have\ X\ mol.}$ $\quad\quad\quad\quad$ *its calculation is above.

X= 1.25 x 10^{-3} mol EDTA

The mole number of SO_4^{2-} is also 1.25 x 10^{-3}.

1 mol SO_4^{2-} $\quad\quad\quad\quad\quad\quad\quad$ is 96 g $\quad\quad\quad\quad$ If 10 mL $\quad\quad\quad$ contain 120 mg SO_4^{2-}

$\underline{1.25\ x\ 10^{-3}\ mol\ SO_4^{2-}}$ $\quad\quad$ is X g. $\quad\quad\quad\quad$ $\underline{100\ mL}$ $\quad\quad\quad\quad$ contain X mg SO_4^{2-}.

X= 1.20 x 10^{-1} g SO_4^{2-}= 120 mg SO_4^{2-} $\quad\quad\quad$ X= 1200 mg SO_4^{2-}/100 mL

Preparation of 0.1 M Magnesium Chloride Solution:

Dissolve about 20.33 g $MgCl_2.6\ H_2O$ in 1.0 L distilled water.

Standardization of $MgCl_2$ Solution:

Transfer 10.0 mL of $MgCl_2$ solution prepared to a conical flask, dilute to 100 mL with distilled water, add 5.0 mL of pH 10 buffer solution and 2-3 drops of Erio-T indicator. Titrate

with standardized EDTA solution until the indicator turns from red to blue and calculate the real molarity of the solution.

There is this equation at the end point:

$M_{MgCl2} = V_{EDTA} \times M_{EDTA} /10$

2.5. Powder Sample Analysis (Calculation of Mass Percentage)

The solid sample is weighed on an analytical balance at around 0.1 (four digits of weight after comma are recorded). Dissolve it with about 50 mL of distilled water and transfer into a conical flask. The percentages of magnesium, zinc or iron contained in the sample are determined by considering complexometric titration analyzes found on the relevant pages of the laboratory data sheet. In order to determine the calcium percentage of sample, the following procedure is used:

Add 3.0 mL of pH 10 buffer solution and 2-3 drops of murexide indicator. Titrate with standardized EDTA solution until the indicator turns redish-pink and note the volume of titrant.

Calculations:

Specimen results:
m_{Sample}= 0.1055 g
M_{EDTA}= 0.1000 M
V_{EDTA}= 10.0 mL

? m Ca $^{2+}$= 10.0 mL EDTA . $\dfrac{0.1000\ mol\ EDTA}{1000\ mL\ EDTA}$. $\dfrac{1\ mol\ Ca^{2+}}{1\ mol\ EDTA}$. $\dfrac{40\ g\ Ca^{2+}}{1\ mol\ Ca^{2+}}$

?   = 0.04 g Ca

For the percentage of Ca in the sample:

0.1055 g sample   contain 0.04 g Ca
100 g sample   contain X g

X= 37.91 g Ca; The solid sample contains 37.91% calcium.

II. Solution Route:

While,

1000 mL of EDTA solution	contain 0.1000 mol of EDTA
10.0 mL of EDTA solution	contain X mol.

$X = 1 \times 10^{-3}$ mol EDTA

The mole number of calcium is also 1×10^{-3}.

If 1 mol Ca	is 40 g,
1×10^{-3} mol Ca	is X g.

$X = 4 \times 10^{-2}$ g Ca

Calculation of mass percentage is made as above.

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Periodic Table of the Elements

atomic number

atomic weight

symbol:

14	28.09
Si	
Silicon	

name

black — solid
blue — liquid
red — gas
white — synthetically prepared

most stable isotope

alkali metals
alkaline earth metals
transitional metals
other metals
nonmetals
noble gases

1	1.01																	2	4.003
H																		He	
Hydrogen																		Helium	

3	6.94	4	9.01			5	10.81	6	12.01	7	14.01	8	15.999	9	18.998	10	20.18
Li		Be				B		C		N		O		F		Ne	
Lithium		Beryllium				Boron		Carbon		Nitrogen		Oxygen		Fluorine		Neon	

11	22.99	12	24.31		13	26.98	14	28.09	15	30.97	16	32.06	17	35.45	18	39.95
Na		Mg			Al		Si		P		S		Cl		Ar	
Sodium		Magnesium			Aluminum		Silicon		Phosphorus		Sulfur		Chlorine		Argon	

19	39.10	20	40.08	21	44.96	22	47.90	23	50.94	24	51.996	25	54.94	26	55.85	27	58.93	28	58.70	29	63.55	30	66.37	31	69.72	32	72.59	33	74.92	34	78.96	35	79.90	36	83.80
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Potassium	Calcium	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc	Gallium	Germanium	Arsenic	Selenium	Bromine	Krypton

37	85.47	38	87.62	39	88.91	40	91.22	41	92.91	42	95.94	43	(98)	44	101.07	45	102.91	46	106.40	47	107.87	48	112.41	49	114.82	50	118.69	51	121.75	52	127.60	53	126.90	54	131.30
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Rubidium	Strontium	Yttrium	Zirconium	Niobium	Molybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium	Indium	Tin	Antimony	Tellurium	Iodine	Xenon

55	132.91	56	137.33	57	138.91	72	178.49	73	180.95	74	183.86	75	186.21	76	190.20	77	192.22	78	196.09	79	196.97	80	200.59	81	204.37	82	207.19	83	208.98	84	(209)	85	(210)	86	(222)
Cs	Ba	La▸	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Cesium	Barium	Lanthanum	Hafnium	Tantalum	Tungsten	Rhenium	Osmium	Iridium	Platinum	Gold	Mercury	Thallium	Lead	Bismuth	Polonium	Astatine	Radon

87	(223)	88	226.03	89	227.03	104	(261)	105	(262)	106	(266)	107	(262)	108	(265)	109	(266)	110	(271)	111	(272)	112	(277)		113	114	(285)	115	116	(289)	117	118	(293)
Fr	Ra	Ac▸	Rf	Ha	Sg	Bh	Hs	Mt				(113)	114	(115)	116	(117)	118
Francium	Radium	Actinium	Rutherfordium	Hahnium	Seaborgium	Bohrium	Hassium	Meitnerium									

58	140.12	59	140.91	60	144.24	61	(145)	62	150.40	63	151.96	64	157.25	65	158.93	66	162.50	67	164.93	68	167.26	69	168.93	70	173.04	71	174.97
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium

90	232.04	91	231.04	92	238.03	93	237.05	94	(244)	95	(243)	96	(247)	97	(247)	98	(251)	99	(252)	100	(257)	101	(260)	102	(259)	103	(262)
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium	Californium	Einsteinium	Fermium	Mendelevium	Nobelium	Lawrencium