



ANALYTICAL CHEMISTRY LABORATORY MANUAL FOR CHEMICAL ENGINEERING



Prof. Dr. Abdürrezzak E. BOZDOĞAN

Prof. Dr. İkbâl KOYUNCU

Prof. Dr. Sezgin BAKIRDERE

Prof. Dr. Bürge AŞÇI

Assoc. Prof. Dr. Özlem AKSU DÖNMEZ

Assoc. Prof. Dr. Özlem YAZICI

Assist. Prof. Dr. Gülten ÇETİN

Dr. Özge GÖRDÜK

Prof. Dr. Yücel ŞAHİN

Prof. Dr. Güzin ALPDOĞAN

Prof. Dr. Hüsnü CANKURTARAN

Prof. Dr. Sevgi KOCAOBA

Assoc. Prof. Dr. Fatma TURAK

Assoc. Prof. Dr. Şule DİNÇ ZOR

Dr. Türkan BÖRKLÜ BUDAK

Res. Asst. Sezin ERARPAT

İSTANBUL, 2021



ANALYTICAL CHEMISTRY LABORATORY MANUAL FOR CHEMICAL ENGINEERING

Prof. Dr. Abdürrezzak E. BOZDOĞAN

Prof. Dr. İkbâl KOYUNCU

Prof. Dr. Sezgin BAKIRDERE

Prof. Dr. Bürge AŞÇI

Assoc. Prof. Dr. Özlem AKSU DÖNMEZ

Assoc. Prof. Dr. Özlem YAZICI

Assist. Prof. Dr. Gülten ÇETİN

Dr. Özge GÖRDÜK

Prof. Dr. Yücel ŞAHİN

Prof. Dr. Güzin ALPDOĞAN

Prof. Dr. Hüsnü CANKURTARAN

Prof. Dr. Sevgi KOCAOBA

Assoc. Prof. Dr. Fatma TURAK

Assoc. Prof. Dr. Şule DİNÇ ZOR

Dr. Türkan BÖRKLÜ BUDAK

Res. Asst. Sezin ERARPAT

İSTANBUL, 2021

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:

TABLE OF CONTENTS

ANALYTICAL CHEMISTRY LABORATORY WORKING GUIDELINES.....	5
GENERAL RULES FOR LABORATORY SAFETY and FIRST AID.....	6
FIRST AID AND SAFETY PRECAUTIONS AGAINST ACCIDENTS IN THE LABORATORY.....	8
LABORATORY EQUIPMENTS	10
1. GRAVIMETRY	14
1.1. Precipitation	14
1.2. Digestion	15
1.3. Filtration	16
1.4. Washing.....	16
1.5. Drying and Igniting	17
1.6. Weighing	18
1.7. Calculation of Result	19
1.8. Gravimetric Determination of Sulfate.....	20
1.9. Gravimetric Determination of Iron	22
2. VOLUMETRY (TITRIMETRY).....	25
2.1. Neutralization Titrations	27
2.1.1. Acidimetry.....	27
2.1.1.1. Determination of Sodium Hydroxide-Sodium Carbonate.....	29
2.1.2. Alkalimetry.....	32
2.1.2.1. Determination of Sulphuric Acid	33
2.2. Redox Titrations.....	33
2.2.1. Manganometry	34
2.2.1.1. Determination of Nitrite Ion.....	36
2.2.1.2. Determination of Oxalate Ion ($\text{C}_2\text{O}_4^{2-}$).....	37
2.2.2. Iodometry	38
2.2.2.1. Determination of Copper.....	39
2.2.3. Bromometry	40
2.2.3.1. Determination of Arsenic(III)	42
2.3. Precipitation Titrations.....	43
2.3.1. Determination of Bromide Ion	43
2.4. Complexometry.....	44
2.4.1. Determination of Magnesium-Zinc	48
2.4.2. Determination of Total Hardness of Water	49
References	51

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.

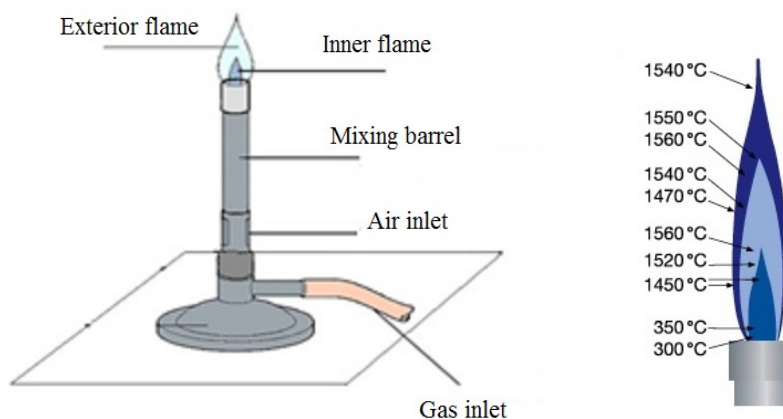


Figure 1. Bunsen burner and its flame.

- 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 treatment 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.

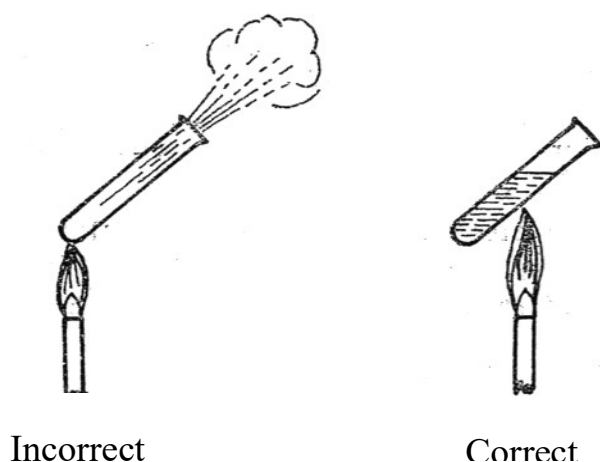


Figure 2. Heating process in tubes.

- 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 (Br₂) 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



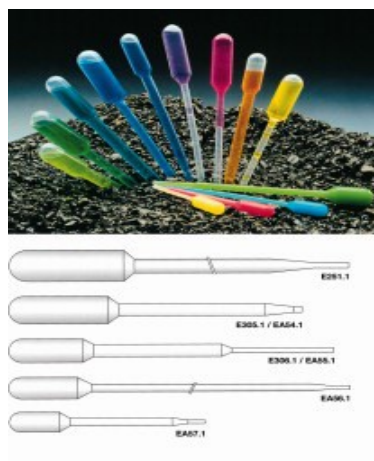
Sheet Foot (tripod)



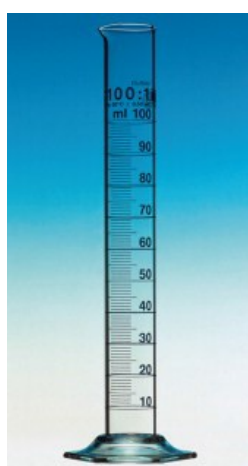
Burner (Bunsen)



Brush



Plastic Pasteur Pipette



Measuring Cylinder



Wash Bottle



Forceps



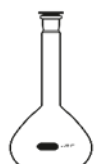
Tube holder and test tubes



Centrifuge Tube



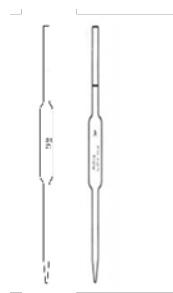
Spatula



Volumetric flask



Pipette



Volumetric pipette



Burette



Desiccator



Crucible tongs



Burette clamp



Support



Funnel

Figure 3. Tools and equipment used in qualitative analysis laboratory.

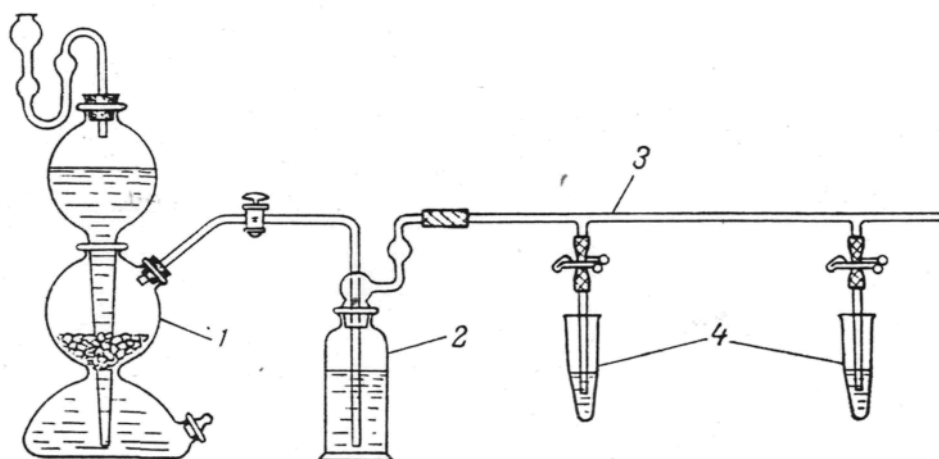


Figure 4. Kipp apparatus used for obtaining hydrogen sulfide gas (1-Kipp apparatus, 2- Washing flask, 3- Hydrogen sulfur gas outlet tube, 4- Tube containing saturated hydrogen sulfide solution).

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 losing amount 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 precipitate 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 $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$ 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 $\frac{2}{3}$ 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:

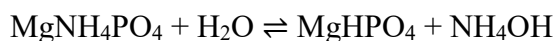
1) Solvents that precipitate in water to dissolve by ionization: These are solutions containing common ions with the precipitate. The co-ion can easily be given in the form of a solution of a volatile compound or precipitate.

For example, the $\text{Fe}(\text{OH})_3$ 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, $\text{Fe}(\text{OH})_3$, 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,



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 pipped 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 $\text{Mg}_2\text{P}_2\text{O}_7$ form. If the required temperature is less than 250°C , the drying process is irritating if it is between 250 and 1200°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

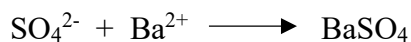
$$X = \frac{142}{233} \times T \text{ g Na}_2\text{SO}_4$$

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. Gravimetric Determination of Sulfate

In an aqueous solution, sulfate ion undergoes the following reaction with barium:



Barium sulfate which forms as a crystalline precipitate, is collected on a suitable filter, washed with water, then ignited and weighed. From the mass of BaSO_4 , the amount of sulfate present in the original sample is calculated.

Gravimetric Analysis:

1. Heating to Constant Weight

Before a precipitate is transferred to a crucible, the crucible should be dried to constant weight at the igniting temperature. For this aim, place the cleaned crucibles in the furnace as required. Allow them to cool in a desiccator and then weigh. Return them to the furnace for 1 hour and repeat the weighing process which should be carried out until two consecutive masses agree to within 0.1 mg.

2. Preparation of 0.10 M Barium Chloride Solution

Weigh 2.5 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ into a conical flask, dissolve with distilled water, transfer to a 100 mL volumetric flask and dilute to the mark with distilled water and mix thoroughly.

3. Process

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 100 mL of distilled water and 5.0 mL of 2.0 M HCl until pH is 2-3 and heat the solution nearly to boiling in a water bath. Acidification prevents to precipitate barium carbonate and phosphate along with BaSO_4 . Heat some BaCl_2 solution in a beaker nearly to boiling and add this solution dropwise with vigorous stirring to the hot sample solution. After precipitation process, digest the precipitated BaSO_4 at below the boiling point for 1-2 hours in the water bath. Mix with a glass rod occasionally.

Precipitation in a weakly acidic medium, heating and mixing the solution provides precipitate to occur in the form of large particles.

Decant the supernatant liquid through a white band filter paper. Wash the precipitate twice by using about 10.0 mL portions of distilled water. 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 900 °C on an electric furnace for ignition. Allow to cool in a desiccator and weigh BaSO₄.

Calculations:

$$T (\text{BaSO}_4) = m_{\text{crucible with precipitate}} - m_{\text{crucible}}$$

$$T \text{ g BaSO}_4 \cdot \frac{1 \text{ mol BaSO}_4}{233 \text{ g BaSO}_4} \cdot \frac{96 \text{ g SO}_4}{1 \text{ mol SO}_4} \cdot \frac{100 \text{ mL}}{25 \text{ mL}} = \dots\dots \text{g sulfate/100 mL}$$

II. Solution Route:

$$T (\text{BaSO}_4) = m_{\text{crucible with precipitate}} - m_{\text{crucible}}$$

While,

233 g BaSO ₄	is formed by 96 g SO ₄	(SO ₄ : 96 g/mol)
T g BaSO ₄	is formed A g SO ₄	(BaSO ₄ : 233 g/mol)

$$A = \frac{96}{233} \times T \text{ g SO}_4$$

While,

25 mL of sample	contain A x 10 ³ mg SO ₄	
100 mL of sample	contain ? mg SO ₄	

The result is found as mg/100 mL.

1.9. Gravimetric Determination of Iron

The hydroxides of the di- and trivalent metals precipitate at pHs below:

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⁺

As seen that Al³⁺ Cr³⁺ Fe³⁺ precipitate in a weakly acidic medium. To form precipitate, those of divalent prefer slightly more basic mediums.

Gravimetric Analysis:

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 NH₄OH solution (1:1, v/v) dropwise until pH reaches 7 in order to precipitate Fe³⁺ 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 NH₄OH. If you detect the appearance of some red-brown precipitate as the drop of the solution moves downward through the solution add an additional NH₄OH solution (control the pH) The reaction is:



in simple terms;

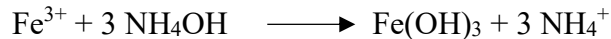


Decant the supernatant liquid through a black band filter paper. Wash the precipitate several times with hot 1% NH_4NO_3 solution (The filtrate must be kept for determination of manganese). Remove the filter paper with precipitate and then place it in a crucible taken to the constant weight. Dry the paper with a small flame and heat the crucible for 15 min at 500 – 550 °C on an electric furnace for ignition. Allow to cool in a desiccator and weigh Fe_2O_3 .



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:



$$T (\text{Fe}_2\text{O}_3) = m_{\text{crucible with precipitate}} - m_{\text{crucible}}$$

$$\begin{aligned} T \text{ g Fe}_2\text{O}_3 & \cdot \frac{1 \text{ mol Fe}_2\text{O}_3}{160 \text{ g Fe}_2\text{O}_3} \cdot \frac{2 \text{ mol Fe}^{3+}}{1 \text{ mol Fe}_2\text{O}_3} \cdot \frac{56 \text{ g Fe}^{3+}}{1 \text{ mol Fe}^{3+}} \cdot \frac{100 \text{ mL}}{25 \text{ mL}} \\ &= \frac{112}{160} \times T \times 4 \text{ g Fe}^{3+}/100 \text{ mL} \end{aligned}$$

II. Solution Route:

$$T (\text{Fe}_2\text{O}_3) = m_{\text{crucible with precipitate}} - m_{\text{crucible}}$$

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)
$A = \frac{112}{160} \times T \text{ g Fe}^{3+}$		

While,

25 mL of sample contain $A \times 10^3 \text{ mg Fe}^{3+}$

100 mL of sample contain ? mg Fe^{3+}

The result is found as $\text{mg}/100 \text{ mL}$

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. H₂SO₄ 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.

M_w: 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

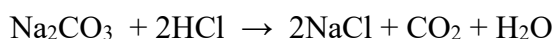
X= 8.29 mL

HCl acid volume calculated is transferred into a volumetric flask, then diluted until 1.0 L with distilled water and mixed 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 Na₂CO₃, NaHCO₃, Na₂B₄O₇, HgO or tiosulphate solutions.

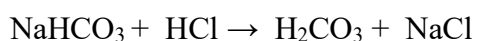
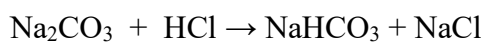
Sodium carbonate is frequently used as a standard material for acid solutions.



Accurately weigh out three 0.1 g samples of dried, anhydrous Na₂CO₃ 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:



Specimen results:

Average of accurate titres: 10.0 mL

Weight of Na₂CO₃= 0,0500 g

$$0.0500 \text{ g Na}_2\text{CO}_3 = 10.0 \text{ mL HCl} \cdot \frac{\text{X mol HCl}}{1000 \text{ mL HCl}} \cdot \frac{1 \text{ mol Na}_2\text{CO}_3}{2 \text{ mol HCl}} \cdot \frac{106 \text{ g Na}_2\text{CO}_3}{1 \text{ mol Na}_2\text{CO}_3}$$

X = 0.0943 M HCl, real concentration of hydrochloric acid solution.

II. Solution Route:

106 g Na₂CO₃ is 1 mole

0.0500 g is X mole.

$$X = 4.72 \times 10^{-4} \text{ mole Na}_2\text{CO}_3$$

According to the reaction above;

1 mole Na₂CO₃ react with 2 mole HCl

4.72x10⁻⁴ mole Na₂CO₃ react with X mole HCl.

$$X = 9.43 \times 10^{-4} \text{ mol HCl}$$

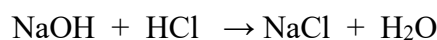
10.0 mL of HCl solution contain 9.43x10⁻⁴ mole HCl, so

1000 mL of HCl solution contain X mole HCl.

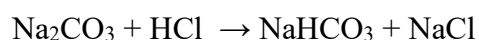
$$X = 0.0943 \text{ mol/L HCl}$$

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 (V₁).



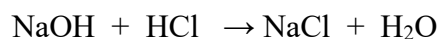
if the volume of HCl solution used in this titration; X mL and



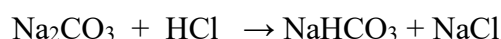
the volume of HCl solution used in this titration; Y mL, then

$$V_1 = X + Y$$

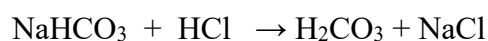
Take another sample containing 25.0 mL of the unknown solution, add 3-5 drops of methyl orange indicator (yellow-orange color, pH: 3.1 - 4.7) and carry the titration until the color turns into red. Boil the solution gently and drive off CO₂. Cool the solution to room temperature under the tap water and carry on the titration till you reach the red end-point. Record again the titrant volume where the indicator changes color (V₂).



if the volume of HCl solution used in this titration; X mL,



the volume of HCl solution used in this titration; Y mL and



again the volume of HCl solution used in this titration; Y mL. Because the mole number of Na₂CO₃ equals to the mole number of NaHCO₃, they require the same volume of HCl solution. If so;

$$V_2 = X + Y + Y$$

Calculations:

In order to titrate NaOH and Na₂CO₃, volumes of standardized HCl solution required:

$$V_{\text{NaOH}} = V_1 - (V_2 - V_1) \quad \text{mL} \quad \{ V_{\text{NaOH}} = (X + Y) - [(X + Y + Y) - (X + Y)] \}$$

$$V_{\text{NaOH}} = X \text{ mL}$$

and

$$V_{\text{Na}_2\text{CO}_3} = 2 \times (V_2 - V_1) \quad \text{mL} \quad \{ V_{\text{Na}_2\text{CO}_3} = 2 \times [(X + Y + Y) - (X + Y)] \}$$

$$V_{\text{Na}_2\text{CO}_3} = 2Y \text{ mL}$$

$$M_{\text{HCl}} = 0.1000 \text{ M}$$

$$M_{\text{WNaOH}} = 40 \text{ g/mol}$$

$$M_{\text{WNa}_2\text{CO}_3} = 106 \text{ g/mol}$$

$$\text{? m NaOH} = X \text{ mL HCl} \cdot \frac{0.1000 \text{ mol HCl}}{1000 \text{ mL HCl}} \cdot \frac{1 \text{ mol NaOH}}{1 \text{ mol HCl}} \cdot \frac{40 \text{ g NaOH}}{1 \text{ mol NaOH}} \cdot \frac{100 \text{ mL}}{25 \text{ mL}}$$

$$? \text{ m Na}_2\text{CO}_3 = 2Y \text{ mL HCl} \cdot \frac{0.1000 \text{ mol HCl}}{1000 \text{ mL HCl}} \cdot \frac{1 \text{ mol Na}_2\text{CO}_3}{2 \text{ mol HCl}} \cdot \frac{106 \text{ g Na}_2\text{CO}_3}{1 \text{ mol Na}_2\text{CO}_3} \cdot \frac{100 \text{ mL}}{25 \text{ mL}}$$

II. Solution Route:

The mole number of NaOH:

$$n_{\text{HCl}} = M_{\text{HCl}} \cdot V_{\text{HCl}} = 0.1000 \cdot X = A \text{ mmol HCl}$$

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 Na₂CO₃:

$$n_{\text{HCl}} = M_{\text{HCl}} \cdot V_{\text{HCl}} = 0.1000 \cdot 2Y = B \text{ mmol}$$

At the end-point, for B mmol HCl, there is B/2 mmol Na₂CO₃. Because 2 mol HCl react with 1 mol Na₂CO₃ 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 (V₁). 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 (V₂).

The volumes of HCl solution required for analytes can be calculated as showed below:

$$V_{\text{NaOH}} = V_1 - V_2 \quad \text{mL} \quad \{ V_{\text{NaOH}} = (X + Y) - (Y) \}$$

$$V_{\text{NaOH}} = X \quad \text{mL} \quad \text{and}$$

$$V_{\text{Na}_2\text{CO}_3} = 2 \times V_2 \quad \text{mL} \quad \{ V_{\text{Na}_2\text{CO}_3} = 2 \times Y \}$$

$$V_{\text{Na}_2\text{CO}_3} = 2Y \quad \text{mL}$$

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:

$$m_{\text{NaOH}} = \frac{0.1 \text{ mol NaOH}}{1 \text{ mol NaOH}} \cdot 40 \text{ g NaOH}$$

$$m_{\text{NaOH}} = 4 \text{ g NaOH}$$

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 label.

$$M_{\text{HCl}} \cdot V_{\text{HCl}} = M_{\text{NaOH}} \cdot V_{\text{NaOH}}$$

2.1.2.1. Determination of Sulphuric Acid

Transfer 25.0 mL of sample solution with a pipette to a conical flask and dilute with distilled water about 75-100 mL. Add 3-5 drops of phenolphthalein indicator and titrate the sample with standard NaOH until the indicator turns pink. Repeat the titration at least three times and record the average of titrant volumes consumed.

Calculation:

$$? \text{ m H}_2\text{SO}_4 = \frac{V \text{ mL NaOH} \cdot 0.1 \text{ mol NaOH} \cdot 1 \text{ mol H}_2\text{SO}_4 \cdot 98 \text{ g H}_2\text{SO}_4 \cdot 100 \text{ mL}}{1000 \text{ mL NaOH} \cdot 2 \text{ mol NaOH} \cdot 1 \text{ mol H}_2\text{SO}_4 \cdot 25 \text{ mL}}$$

II. Solution Route:

The mole number of H_2SO_4 :

$$n_{\text{NaOH}} = M_{\text{NaOH}} \cdot V_{\text{NaOH}} = 0.1 \cdot V = A \text{ mmol NaOH}$$

At the end-point, for A mmol NaOH, there is A/2 mmol H_2SO_4 .

1 mmol H_2SO_4	is 98 mg	If 25 mL of sample	contain 49A mg H_2SO_4 ,
A/2 mmol H_2SO_4	is 49A mg.	100 mL of sample	contain 4 x 49A mg H_2SO_4 .

Report the result 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.

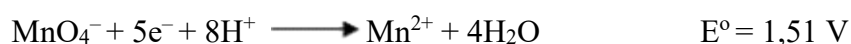
Titration performed by oxidation and reduction reactions are called redox titration. If the solution used in the titration is an oxidizing agent solution, the analytical method is called

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



b) In weak acidic, weak basic and neutral mediums



c) In strong basic mediums



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 Permanganate Solution

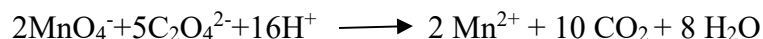
Weigh out 3.16 g of KMnO_4 (Mw: 158 g/mol) and dissolve it in 1.0 L of distilled water. Heat to boiling and keep hot for about 15-30 min. After cooling, filter the solution through a fine-porosity filtering crucible. Transfer the solution to a clean glass-stoppered dark bottle and keep away from sunlight.

Standardization of 0.02 M KMnO_4 Solution with Sodium Oxalate

As_2O_3 , KI, iron wire, $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$, $\text{Na}_2\text{C}_2\text{O}_4$ or $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ can be used to determine the exact concentration of the KMnO_4 solution.

Dry $\text{Na}_2\text{C}_2\text{O}_4$ for at least 1 h at 105-110 °C and cool in a desiccator. Dissolve 0.1 g of the dried $\text{Na}_2\text{C}_2\text{O}_4$ 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.



Calculations:

Chemical reaction above is observed in the titration of $\text{Na}_2\text{C}_2\text{O}_4$ with KMnO_4 under acidic conditions.

Specimen results:

Average of accurate titres (V_{KMnO_4}): 15.0 mL

Weight of $\text{Na}_2\text{C}_2\text{O}_4 = 0.1000 \text{ g}$

$$0.1000 \text{ g Na}_2\text{C}_2\text{O}_4 = 15.0 \text{ mL KMnO}_4 \cdot \frac{\text{X mol KMnO}_4}{1000 \text{ mL KMnO}_4} \cdot \frac{5 \text{ mol Na}_2\text{C}_2\text{O}_4}{2 \text{ mol KMnO}_4} \cdot \frac{134 \text{ g Na}_2\text{C}_2\text{O}_4}{1 \text{ mol Na}_2\text{C}_2\text{O}_4}$$

$X = 0.0198 \text{ M KMnO}_4$, real concentration of the solution.

II. Solution Route:

While,

134 g $\text{Na}_2\text{C}_2\text{O}_4$ is 1 mol

0.1000 g is X mol.

$$X = 7.46 \times 10^{-4} \text{ mol Na}_2\text{C}_2\text{O}_4$$

According to the reaction above;

2 mol of KMnO_4 react with 5 mol of $\text{C}_2\text{O}_4^{2-}$, then

X mol of KMnO_4 react with $7.46 \times 10^{-4} \text{ mol C}_2\text{O}_4^{2-}$.

$X = 2.98 \times 10^{-4} \text{ mol}$ of KMnO_4 is required.

15.0 mL of KMnO_4 solution have $2.98 \times 10^{-4} \text{ mol}$ of KMnO_4

1000 mL of KMnO_4 solution have X mol of KMnO_4 .

$$X = 0.0198 \text{ mol/L KMnO}_4 = 0.0198 \text{ M KMnO}_4$$

2.2.1.1. Determination of Nitrite Ion

Nitrite ion under acidic conditions transforms as follows:



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.



Calculations:

Calculate the amount of nitrite according to chemical reaction above.

Specimen results:

Average of the sample volumes consumed: 10.0 mL

$$M_{\text{KMnO}_4} = 0.0200 \text{ M}$$

$$V_{\text{KMnO}_4} = 5.0 \text{ mL}$$

$$M_{\text{wNO}_2} = 46 \text{ g/mol}$$

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.

$$? \text{ m}_{\text{NO}_2} = 50 \text{ mL KMnO}_4 \cdot \frac{0.0200 \text{ mol KMnO}_4}{1000 \text{ mL KMnO}_4} \cdot \frac{5 \text{ mol NO}_2^-}{2 \text{ mol KMnO}_4} \cdot \frac{46 \text{ g NO}_2^-}{1 \text{ mol NO}_2^-}$$

$$\text{m}_{\text{NO}_2} = 115 \text{ mg/100mL}$$

II. Solution Route:

While,

1000 mL of KMnO_4 solution have 0.0200 mol of KMnO_4 ,

50 mL of KMnO_4 solution have X mol of KMnO_4 .

$$X = 1 \times 10^{-3} \text{ mol } \text{KMnO}_4$$

According to the reaction occurred,

2 mol KMnO_4 react with 5 mol NO_2^- , then

1×10^{-3} mol KMnO_4 react with X mol NO_2^- .

$$X = 2.5 \times 10^{-3} \text{ mol } \text{NO}_2^-$$

1 mol NO_2^- is 46 g

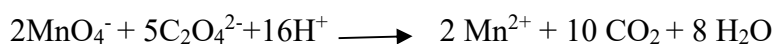
2.5×10^{-3} mol NO_2^- is X g.

$$X = 0.115 \text{ g} = 115 \text{ mg } \text{NO}_2^-/100 \text{ mL}$$

2.2.1.2. Determination of Oxalate Ion ($\text{C}_2\text{O}_4^{2-}$)

Transfer 25.0 mL of sample solution with a pipette to a conical flask and dilute with distilled water about 100 mL. Add 10.0 mL of 1.0 M H_2SO_4 and heat the content of the sample up to 80-90 °C. Fill the burette with KMnO_4 solution and titrant is slowly added to hot 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 oxalate according to chemical reaction above.

Specimen results:

Average of the titrant volumes consumed (V_{KMnO_4}): 5.0 mL

$$M_{\text{KMnO}_4} = 0.0200 \text{ M}$$

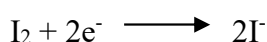
$$M_{\text{W}_{\text{C}_2\text{O}_4}} = 88 \text{ g/mol}$$

$$? \text{ m C}_2\text{O}_4^{2-} = 5.0 \text{ mL KMnO}_4 \cdot \frac{0.0200 \text{ mol KMnO}_4}{1000 \text{ mL KMnO}_4} \cdot \frac{5 \text{ mol Na}_2\text{C}_2\text{O}_4}{2 \text{ mol KMnO}_4} \cdot \frac{88 \text{ g C}_2\text{O}_4^{2-}}{1 \text{ mol C}_2\text{O}_4^{2-}} \cdot \frac{100 \text{ mL}}{25 \text{ mL}}$$

$$= 88 \text{ mg C}_2\text{O}_4^{2-}/100 \text{ mL}$$

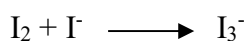
2.2.2. Iodometry

Iodine, which is an oxidizing agent, reduces itself to iodide while oxidizing others in its reactions.

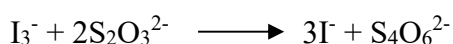


Titration using adjusted iodine solution is called iodimetry, the titration using quantitation of an oxidant performed by titration of iodine, which results from reaction of an oxidizing agent with iodide, with thiosulphate solution is called iodometry.

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:



When the emerging triiodide/iodine is titrated with the adjusted thiosulfate solution,



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 $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$; $M_A=248,19$ 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.

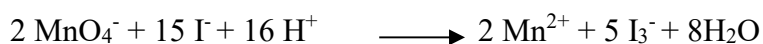
Standardization of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ Solution

$\text{Na}_2\text{S}_2\text{O}_3$ is not a primary standard and thus a freshly prepared solution of this chemical must be standardized. For this purpose, primary standards ($\text{K}_2\text{Cr}_2\text{O}_7$, 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 $\text{Na}_2\text{S}_2\text{O}_3$ 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 $\text{Na}_2\text{S}_2\text{O}_3$ solution prepared and after 10 min, titration is carried out until the single drop of $\text{Na}_2\text{S}_2\text{O}_3$ makes the solution colorless. Repeat the titration at least three times, find the average of titrant volumes and calculate the real molarity of the $\text{Na}_2\text{S}_2\text{O}_3$ solution. Record the value on the bottle label.

Chemical reactions occurred between KMnO_4 and KI and during titration may be represented as:



There is this equation at the end point:

$$M_{\text{KMnO}_4} \times V_{\text{KMnO}_4} = M_{\text{Na}_2\text{S}_2\text{O}_3} \times V_{\text{Na}_2\text{S}_2\text{O}_3}$$

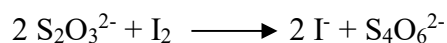
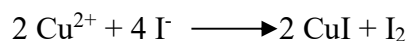
2.2.2.1. Determination of Copper

Transfer 25.0 mL of the sample solution into a conical flask, dilute it with 50 mL of distilled water and adjust pH to 4-4.5 with diluted CH_3COOH solution. Add 1 g of solid KI or 10 mL of 10% KI solution. After 1-2 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 reactions occurred are:



Calculate the amount of copper according to chemical reactions above.

Specimen results:

Average of the titrant volumes consumed ($V_{\text{Na}_2\text{S}_2\text{O}_3}$): 10.0 mL

$M_{\text{Na}_2\text{S}_2\text{O}_3} = 0.1000 \text{ M}$

$M_{\text{Cu}} = 65 \text{ g/mol}$

$$\begin{aligned} ? \text{ m Cu}^{2+} &= 10.0 \text{ mL Na}_2\text{S}_2\text{O}_3 \cdot \frac{0.1000 \text{ mol Na}_2\text{S}_2\text{O}_3}{1000 \text{ mL Na}_2\text{S}_2\text{O}_3} \cdot \frac{1 \text{ mol Cu}^{2+}}{1 \text{ mol Na}_2\text{S}_2\text{O}_3} \cdot \frac{64 \text{ g Cu}^{2+}}{1 \text{ mol Cu}^{2+}} \cdot \frac{100 \text{ mL}}{25 \text{ mL}} \\ &= 0.256 \text{ g Cu}^{2+}/100 \text{ mL} \end{aligned}$$

2.2.3. Bromometry

The relatively high standard oxidation strength of a redox couple $\text{BrO}_3^-/\text{Br}^-$ system ($E^0 = +1.44 \text{ V}$) 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:



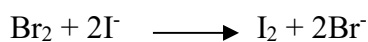
As (III), Sb (III), Sn (II), Tl (I), $\text{Fe}(\text{CN})_6^{4-}$, hydrazine and many other reducing agents can be directly titrated with the bromate solution and they are determined. Direct titrations with KBrO_3 are performed in the presence of indicators such as methyl orange, methyl reds, etc.

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.



Without reaction, the excess bromine is reacted with excess KI and the iodine released is titrated with the thiosulfate solution.



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.

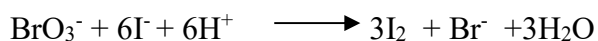
Preparation of 0.02 M Potassium Bromate Solution

Dry potassium bromate at 120°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 $\text{Na}_2\text{S}_2\text{O}_3$ solution and after 10 min, titration is carried out until the single drop of $\text{Na}_2\text{S}_2\text{O}_3$ makes the solution colorless. Repeat the titration at least three times and find the average of titrant volumes.

Chemical reactions occurred between BrO_3^- and I^- and during titration as follows:



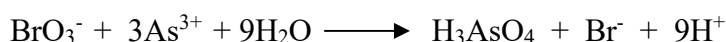
Calculate the real molarity of the KBrO_3 solution.

$$M_{\text{Na}_2\text{S}_2\text{O}_3} \times V_{\text{Na}_2\text{S}_2\text{O}_3} = M_{\text{KBrO}_3} \times V_{\text{KBrO}_3}$$

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 KBrO₃ solution till the indicator turns colorless. Repeat the titration at least three times and record the average of titrant volumes consumed.

Calculations:



Specimen results:

Average of the titrant volumes consumed (V_{KBrO_3}): 10.0 mL

$$M_{\text{KBrO}_3} = 0.0200 \text{ M}$$

$$M_{\text{W As}^{3+}} = 75 \text{ g/mol}$$

$$? \text{ m As}^{3+} = 10.0 \text{ mL KBrO}_3 \cdot \frac{0.0200 \text{ mol KBrO}_3}{1000 \text{ mL KBrO}_3} \cdot \frac{3 \text{ mol As}^{3+}}{1 \text{ mol KBrO}_3} \cdot \frac{75 \text{ g As}^{3+}}{1 \text{ mol As}^{3+}} \cdot \frac{100 \text{ mL}}{25 \text{ mL}}$$

$$? = 180 \text{ mg As}^{3+} / 100 \text{ mL}$$

II. Solution Route:

While,

1000 mL of KBrO₃ solution have 0.0200 mol of KBrO₃

10.0 mL KBrO₃ solution have X mol.

$$X = 2 \times 10^{-4} \text{ mol KBrO}_3$$

1 mol BrO₃⁻ react with 3 mol As³⁺,

2 x 10⁻⁴ mol BrO₃⁻ react with X mol As³⁺.

$$X = 6 \times 10^{-4} \text{ mol As}^{3+}$$

1 mol As³⁺ is 75 g

6 x 10⁻⁴ mol As³⁺ is X g.

$$X = 4.5 \times 10^{-2} \text{ g As}^{3+} = 45 \text{ mg As}^{3+}$$

If 25 mL contain 45 mg of As³⁺,

100 mL contain X mg As³⁺.

$$X = 180 \text{ mg As}^{3+} / 100 \text{ mL}$$

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 Silver 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 $250\text{-}350^\circ\text{C}$ 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.



Calculations:

$$2.923/20 = 0.1461 \text{ g NaCl} = V \text{ mL AgNO}_3 \cdot \frac{X \text{ mol AgNO}_3}{1000 \text{ mL AgNO}_3} \cdot \frac{58.44 \text{ g NaCl}}{1 \text{ mol NaCl}} = \dots \text{M AgNO}_3$$

2.3.1. Determination of Bromide Ion

Pipette accurately 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 occurred during titration:



Specimen results:

$$M_{\text{AgNO}_3} = 0.1000 \text{ M}$$

$$V_{\text{AgNO}_3} = 10.0 \text{ mL}$$

$$M_{\text{WBr}} = 80 \text{ g/mol}$$

$$? \text{ m Br}^- = 10.0 \text{ mL AgNO}_3 \cdot \frac{0.1000 \text{ mol AgNO}_3}{1000 \text{ mL AgNO}_3} \cdot \frac{1 \text{ mol Br}^-}{1 \text{ mol AgNO}_3} \cdot \frac{80 \text{ g Br}^-}{1 \text{ mol Br}^-} \cdot \frac{100 \text{ mL}}{25 \text{ mL}}$$

$$? = 320 \text{ mg Br}^-/100 \text{ mL}$$

II. Solution Route:

While,

1000 mL of AgNO₃ solution have 0.1000 mol of AgNO₃

10.0 mL of AgNO₃ solution have X mol.

$$X = 1 \times 10^{-3} \text{ mol AgNO}_3$$

At the end of the titration, the mole number of AgNO₃ 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⁻.

$$X = 8.0 \times 10^{-2} \text{ g Br}^- = 80 \text{ mg Br}^-$$

$$X = 320 \text{ mg Br}^-/100 \text{ mL}$$

2.4. Complexometry

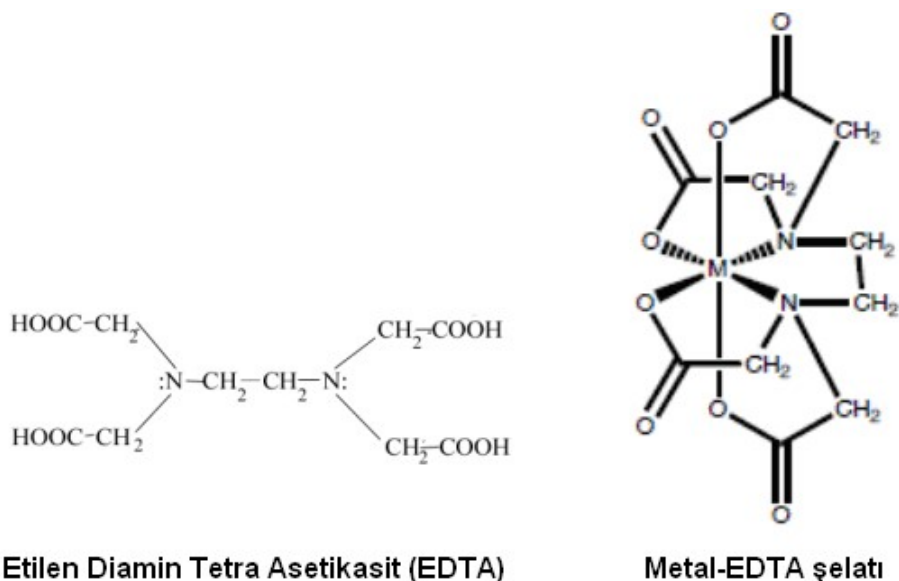
The new structure formed by one or more central atoms and charged or uncharged ion called the ligands attached to them or ion groups or molecules, is called **complex**. If the central atom is one, it is called a mononuclear complex, and if the central atom is a few, it is called polynuclear complexes. 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(NH₃)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**.

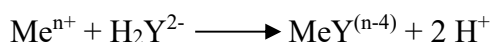
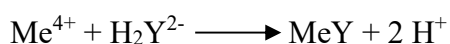
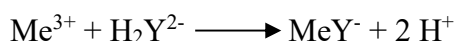
EDTA Titrations

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.



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 (HY₄) and disodium salt is shown as (Na₂H₂Y.2H₂O). The ions in aqueous solution are also shown as H₂Y²⁻. The reaction of this ion with metal ions of different valence is as given below.



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 distilled 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 $\text{Na}_2\text{H}_2\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2 \cdot 2\text{H}_2\text{O}$ 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 ($C_{\text{Fe}}=14 \text{ mg/mL}$) 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:

$$m_{\text{Fe}^{3+}} = 14 \text{ mg}$$

$$V_{\text{EDTA}} = 2.6 \text{ mL}$$

$$0.014 \text{ g Fe} = 2.6 \text{ mL EDTA} \cdot \underline{X \text{ mol EDTA}} \cdot \frac{1 \text{ mol Fe}}{1000 \text{ mL EDTA}} \cdot \frac{56 \text{ g Fe}}{1 \text{ mol EDTA}} \cdot \frac{1 \text{ mol Fe}}{1 \text{ mol Fe}}$$

$$X = 0.0961 \text{ M}$$

II. Solution Route:

While,

$$56 \text{ g Fe} \quad \text{is } 1 \text{ mol}$$

$$\underline{0.014 \text{ g Fe} \quad \text{is } X \text{ mol.}}$$

$$X = 2.5 \times 10^{-4} \text{ mol Fe}$$

At the end of the titration, the mole number of EDTA is 2.5×10^{-4} .

$$\text{If } 2.6 \text{ mL of EDTA solution} \quad \text{contain } 2.5 \times 10^{-4} \text{ mol of EDTA}$$

$$\underline{1000 \text{ mL of EDTA solution} \quad \text{contain } X \text{ mol of EDTA.}}$$

$$X = 0.0961 \text{ mol/L EDTA}$$

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. Fluoride, cyanide, hydroxide, sulfosalicylic acid, tartarate, citrate, ammonium and iodide can be used as a masking agent.

Calculations:

Specimen results:

$$M_{\text{EDTA}} = 0.1000 \text{ M}, V_1 = 10.0 \text{ mL}, V_2 = 4.0 \text{ mL}$$

$$V_2 = V_{\text{Zn}} = 4.0 \text{ mL},$$

$$V_1 - V_2 = V_{\text{Mg}} = 10.0 - 4.0 = 6.0 \text{ mL}.$$

$$\text{? m Zn}^{2+} = 4.0 \text{ mL EDTA} \cdot \frac{0.1000 \text{ mol EDTA}}{1000 \text{ mL EDTA}} \cdot \frac{1 \text{ mol Zn}^{2+}}{1 \text{ mol EDTA}} \cdot \frac{65 \text{ g Zn}^{2+}}{1 \text{ mol Zn}^{2+}} \cdot \frac{100 \text{ mL}}{20 \text{ mL}}$$

$$\text{?} = 130 \text{ mg Zn}^{2+}/100 \text{ mL}$$

$$\text{? m Mg}^{2+} = 6.0 \text{ mL EDTA} \cdot \frac{0.1000 \text{ mol EDTA}}{1000 \text{ mL EDTA}} \cdot \frac{1 \text{ mol Mg}^{2+}}{1 \text{ mol EDTA}} \cdot \frac{24 \text{ g Mg}^{2+}}{1 \text{ mol Mg}^{2+}} \cdot \frac{100 \text{ mL}}{20 \text{ mL}}$$

$$\text{?} = 72 \text{ mg Mg}^{2+}/100 \text{ mL}$$

II. Solution Route:

1000 mL of EDTA solution have 0.1000 mol of EDTA

4.0 mL EDTA solution have X mol.

$$X = 4 \times 10^{-4} \text{ mol EDTA}$$

At the end of the titration, the mole number of Zn^{2+} is 4×10^{-4} .

1 mol Zn^{2+} is 65 g

If 20 mL contain 26 mg of Zn^{2+} ,

4×10^{-4} mol Zn^{2+} is X g.

100 mL contain X mg Zn^{2+} .

$$X = 2.6 \times 10^{-2} \text{ g } \text{Zn}^{2+} = 26 \text{ mg } \text{Zn}^{2+}$$

$$X = 130 \text{ mg } \text{Zn}^{2+}/100 \text{ mL}$$

1000 mL of EDTA solution have 0.1000 mol of EDTA

6.0 mL EDTA çözeltisinde have X mol.

$$X = 6 \times 10^{-4} \text{ mol EDTA}$$

At the end of the titration, the mole number of Mg^{2+} is 6×10^{-4} .

1 mol Mg^{2+} is 24 g

If 20 mL contain 14.4 mg of Mg^{2+}

6×10^{-4} mol Mg^{2+} is X g.

100 mL contain X mg Mg^{2+} .

$$X = 1.44 \times 10^{-2} \text{ g } \text{Mg}^{2+} = 14.4 \text{ mg } \text{Mg}^{2+}$$

$$X = 72 \text{ mg } \text{Mg}^{2+}/100 \text{ mL}$$

2.4.2. Determination of Total Hardness of Water

There are two types of hardness in water samples:

1. Temporary Hardness
2. Permanent Hardness

Temporary hardness is usually caused by the thermally unstable magnesium hydrogencarbonate and calcium hydrogencarbonate dissolved in the water from geological formations like limestone or chalk. Temporary hard water can be softened by boiling the water. Permanent hardness is caused by very soluble magnesium sulfate and slightly soluble calcium sulfate. Permanently hard water cannot be softened by boiling. Regardless of anion type, the total concentration of hardness sources is known as total hardness and it is expressed with equivalent to CaCO_3 or CaO .

1 France Degree (L); 10 mg/L CaCO_3 or 8.4 mg/L MgCO_3

1 German Degree (L); 10 mg/L CaO or 7.13 mg/L MgO

1 England Degree (L); 17.5 mg/L CaCO_3 or 14.7 mg/L MgCO_3

Titration:

Total Hardness of Water: Take 25.0 mL of the water sample into a conical flask, add 1.0 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.

Temporary Hardness: Take 25.0 mL of the water sample into a conical flask and add 3-4 drops of methyl orange indicator. Titrate with standardized HCl solution to the end point.

Permanent Hardness = Total Hardness of Water - Temporary Hardness

References

1. Vogel, A. (1972) Quantitative Inorganic Analysis.
2. Alexeyev, V. (1979) Quantitative Analysis, Mir Publishers.
3. Lurie, J. (1975) Handbook of Analytical Chemistry, Mir Publishers.
4. Afşar, H. (2009) Temel Analitik Kimya.
5. Gündüz, T. (1983) Kantitatif Analiz Laboratuvar Kitabı.
6. Dölen, E. (1988) Analitik Kimya.
7. Apak, M.R. (1997) Temel Analitik Kimya.

Periodic Table of the Elements

1 1.01 H Hydrogen	3 6.94 Li Lithium	4 9.01 Be Beryllium	5 10.81 B Boron	6 12.01 C Carbon	7 14.01 N Nitrogen	8 15.999 O Oxygen	9 18.998 F Fluorine	10 20.18 Ne Neon
11 22.99 Na Sodium	12 24.31 Mg Magnesium	13 26.98 Al Aluminum	14 28.09 Si Silicon	15 30.97 P Phosphorus	16 32.06 S Sulfur	17 35.45 Cl Chlorine	18 39.95 Ar Argon	19 39.10 K Potassium
20 40.08 Ca Calcium	21 44.96 Sc Scandium	22 47.88 Ti Titanium	23 50.94 V Vanadium	24 50.94 Cr Chromium	25 51.996 Mn Manganese	26 55.85 Fe Iron	27 58.93 Co Cobalt	28 58.71 Ni Nickel
37 85.47 Rb Rubidium	38 87.62 Sr Strontium	39 88.91 Y Yttrium	40 91.22 Zr Zirconium	41 92.91 Nb Niobium	42 95.94 Mo Molybdenum	43 98 Tc Technetium	44 101.07 Ru Ruthenium	45 102.91 Rh Rhodium
55 132.91 Cs Cesium	56 137.33 Ba Barium	57 138.91 La Lanthanum	72 178.49 Hf Hafnium	73 180.95 Ta Tantalum	74 183.85 W Tungsten	75 186.21 Re Rhenium	76 186.21 Os Osmium	77 192.22 Ir Iridium
87 223 Fr Francium	88 226.03 Ra Radium	89 227.03 Ac Actinium	104 261 Rf Rutherfordium	105 262 Ha Hahnium	106 266 Sg Seaborgium	107 269 Bh Bohrium	108 269 Hs Hassium	109 269 Mt Meitnerium
118 293 Rn Radon	119 293 Fr Francium	120 293 Ra Radium	121 293 Ac Actinium	122 293 Th Thorium	123 293 Pa Protactinium	124 293 U Uranium	125 293 Np Neptunium	126 293 Pu Plutonium
127 293 At Astatine	128 293 Rn Radon	129 293 Fr Francium	130 293 Ra Radium	131 293 Ac Actinium	132 293 Th Thorium	133 293 Pa Protactinium	134 293 U Uranium	135 293 Np Neptunium
136 293 Po Polonium	137 293 At Astatine	138 293 Rn Radon	139 293 Fr Francium	140 293 Ra Radium	141 293 Ac Actinium	142 293 Th Thorium	143 293 Pa Protactinium	144 293 U Uranium
145 293 Bi Bismuth	146 293 Po Polonium	147 293 At Astatine	148 293 Rn Radon	149 293 Fr Francium	150 293 Ra Radium	151 293 Ac Actinium	152 293 Th Thorium	153 293 Pa Protactinium
154 293 Pb Lead	155 293 Bi Bismuth	156 293 Po Polonium	157 293 At Astatine	158 293 Rn Radon	159 293 Fr Francium	160 293 Ra Radium	161 293 Ac Actinium	162 293 Th Thorium
163 293 Tl Thallium	164 293 Pb Lead	165 293 Bi Bismuth	166 293 Po Polonium	167 293 At Astatine	168 293 Rn Radon	169 293 Fr Francium	170 293 Ra Radium	171 293 Ac Actinium
172 293 Hg Mercury	173 293 Tl Thallium	174 293 Pb Lead	175 293 Bi Bismuth	176 293 Po Polonium	177 293 At Astatine	178 293 Rn Radon	179 293 Fr Francium	180 293 Ra Radium
181 293 Ag Silver	182 293 Cd Cadmium	183 293 In Indium	184 293 Sn Tin	185 293 Sb Antimony	186 293 Te Tellurium	187 293 I Iodine	188 293 Xe Xenon	189 293 Kr Krypton
191 293 Cu Copper	192 293 Zn Zinc	193 293 Ga Gallium	194 293 Ge Germanium	195 293 As Arsenic	196 293 Se Selenium	197 293 Br Bromine	198 293 Kr Krypton	199 293 Rb Rubidium
201 293 Ni Nickel	202 293 Cu Copper	203 293 Zn Zinc	204 293 Ga Gallium	205 293 Ge Germanium	206 293 As Arsenic	207 293 Se Selenium	208 293 Br Bromine	209 293 Kr Krypton
211 293 Co Cobalt	212 293 Ni Nickel	213 293 Cu Copper	214 293 Zn Zinc	215 293 Ga Gallium	216 293 Ge Germanium	217 293 As Arsenic	218 293 Se Selenium	219 293 Br Bromine
221 293 Fe Iron	222 293 Co Cobalt	223 293 Ni Nickel	224 293 Cu Copper	225 293 Zn Zinc	226 293 Ga Gallium	227 293 Ge Germanium	228 293 As Arsenic	229 293 Se Selenium
231 293 Mn Manganese	232 293 Fe Iron	233 293 Co Cobalt	234 293 Ni Nickel	235 293 Cu Copper	236 293 Zn Zinc	237 293 Ga Gallium	238 293 Ge Germanium	239 293 As Arsenic
241 293 Cr Chromium	242 293 Mn Manganese	243 293 Fe Iron	244 293 Co Cobalt	245 293 Ni Nickel	246 293 Cu Copper	247 293 Zn Zinc	248 293 Ga Gallium	249 293 Ge Germanium
251 293 V Vanadium	252 293 Cr Chromium	253 293 Mn Manganese	254 293 Fe Iron	255 293 Co Cobalt	256 293 Ni Nickel	257 293 Cu Copper	258 293 Zn Zinc	259 293 Ga Gallium
261 293 Ti Titanium	262 293 V Vanadium	263 293 Cr Chromium	264 293 Mn Manganese	265 293 Fe Iron	266 293 Co Cobalt	267 293 Ni Nickel	268 293 Cu Copper	269 293 Zn Zinc
271 293 Sc Scandium	272 293 Ti Titanium	273 293 V Vanadium	274 293 Cr Chromium	275 293 Mn Manganese	276 293 Fe Iron	277 293 Co Cobalt	278 293 Ni Nickel	279 293 Cu Copper
281 293 Ca Calcium	282 293 Sc Scandium	283 293 Ti Titanium	284 293 V Vanadium	285 293 Cr Chromium	286 293 Mn Manganese	287 293 Fe Iron	288 293 Co Cobalt	289 293 Ni Nickel
291 293 Na Sodium	292 293 Ca Calcium	293 293 Sc Scandium	294 293 Ti Titanium	295 293 V Vanadium	296 293 Cr Chromium	297 293 Mn Manganese	298 293 Fe Iron	299 293 Co Cobalt
301 293 Li Lithium	302 293 Na Sodium	303 293 Ca Calcium	304 293 Sc Scandium	305 293 Ti Titanium	306 293 V Vanadium	307 293 Cr Chromium	308 293 Mn Manganese	309 293 Fe Iron
311 293 H Hydrogen	312 293 He Helium	313 293 Li Lithium	314 293 Be Beryllium	315 293 B Boron	316 293 C Carbon	317 293 N Nitrogen	318 293 O Oxygen	319 293 F Fluorine
321 293 Ne Neon	322 293 Ar Argon	323 293 K Potassium	324 293 Ca Calcium	325 293 Sc Scandium	326 293 Ti Titanium	327 293 V Vanadium	328 293 Cr Chromium	329 293 Mn Manganese
331 293 Al Aluminum	332 293 Si Silicon	333 293 P Phosphorus	334 293 S Sulfur	335 293 Cl Chlorine	336 293 Ar Argon	337 293 K Potassium	338 293 Ca Calcium	339 293 Sc Scandium
341 293 Br Bromine	342 293 Kr Krypton	343 293 Rb Rubidium	344 293 Sr Strontium	345 293 Y Yttrium	346 293 Zr Zirconium	347 293 Nb Niobium	348 293 Mo Molybdenum	349 293 Tc Technetium
351 293 I Iodine	352 293 Xe Xenon	353 293 Cs Cesium	354 293 Ba Barium	355 293 La Lanthanum	356 293 Ce Cerium	357 293 Pr Praseodymium	358 293 Nd Neodymium	359 293 Pm Promethium
361 293 At Astatine	362 293 Rn Radon	363 293 Fr Francium	364 293 Ra Radium	365 293 Ac Actinium	366 293 Th Thorium	367 293 Pa Protactinium	368 293 U Uranium	369 293 Np Neptunium
371 293 Lu Lutetium	372 293 Yb Ytterbium	373 293 Tm Thulium	374 293 Er Erbium	375 293 Ho Holmium	376 293 Dy Dysprosium	377 293 Tb Terbium	378 293 Gd Gadolinium	379 293 Eu Europium
381 293 La Lanthanum	382 293 Ce Cerium	383 293 Pr Praseodymium	384 293 Nd Neodymium	385 293 Pm Promethium	386 293 Sm Samarium	387 293 Eu Europium	388 293 Gd Gadolinium	389 293 Tb Terbium
391 293 Lu Lutetium	392 293 Yb Ytterbium	393 293 Tm Thulium	394 293 Er Erbium	395 293 Ho Holmium	396 293 Dy Dysprosium	397 293 Tb Terbium	398 293 Gd Gadolinium	399 293 Eu Europium
401 293 Lu Lutetium	402 293 Yb Ytterbium	403 293 Tm Thulium	404 293 Er Erbium	405 293 Ho Holmium	406 293 Dy Dysprosium	407 293 Tb Terbium	408 293 Gd Gadolinium	409 293 Eu Europium
411 293 Lu Lutetium	412 293 Yb Ytterbium	413 293 Tm Thulium	414 293 Er Erbium	415 293 Ho Holmium	416 293 Dy Dysprosium	417 293 Tb Terbium	418 293 Gd Gadolinium	419 293 Eu Europium
421 293 Lu Lutetium	422 293 Yb Ytterbium	423 293 Tm Thulium	424 293 Er Erbium	425 293 Ho Holmium	426 293 Dy Dysprosium	427 293 Tb Terbium	428 293 Gd Gadolinium	429 293 Eu Europium
431 293 Lu Lutetium	432 293 Yb Ytterbium	433 293 Tm Thulium	434 293 Er Erbium	435 293 Ho Holmium	436 293 Dy Dysprosium	437 293 Tb Terbium	438 293 Gd Gadolinium	439 293 Eu Europium
441 293 Lu Lutetium	442 293 Yb Ytterbium	443 293 Tm Thulium	444 293 Er Erbium	445 293 Ho Holmium	446 293 Dy Dysprosium	447 293 Tb Terbium	448 293 Gd Gadolinium	449 293 Eu Europium
451 293 Lu Lutetium	452 293 Yb Ytterbium	453 293 Tm Thulium	454 293 Er Erbium	455 293 Ho Holmium	456 293 Dy Dysprosium	457 293 Tb Terbium	458 293 Gd Gadolinium	459 293 Eu Europium
461 293 Lu Lutetium	462 293 Yb Ytterbium	463 293 Tm Thulium	464 293 Er Erbium	465 293 Ho Holmium	466 293 Dy Dysprosium	467 293 Tb Terbium	468 293 Gd Gadolinium	469 293 Eu Europium
471 293 Lu Lutetium	472 293 Yb Ytterbium	473 293 Tm Thulium	474 293 Er Erbium	475 293 Ho Holmium	476 293 Dy Dysprosium	477 293 Tb Terbium	478 293 Gd Gadolinium	479 293 Eu Europium
481 293 Lu Lutetium	482 293 Yb Ytterbium	483 293 Tm Thulium	484 293 Er Erbium	485 293 Ho Holmium	486 293 Dy Dysprosium	487 293 Tb Terbium	488 293 Gd Gadolinium	489 293 Eu Europium
491 293 Lu Lutetium	492 293 Yb Ytterbium	493 293 Tm Thulium	494 293 Er Erbium	495 293 Ho Holmium	496 293 Dy Dysprosium	497 293 Tb Terbium	498 293 Gd Gadolinium	499 293 Eu Europium
501 293 Lu Lutetium	502 293 Yb Ytterbium	503 293 Tm Thulium	504 293 Er Erbium	505 293 Ho Holmium	506 293 Dy Dysprosium	507 293 Tb Terbium	508 293 Gd Gadolinium	509 293 Eu Europium
511 293 Lu Lutetium	512 293 Yb Ytterbium	513 293 Tm Thulium	514 293 Er Erbium	515 293 Ho Holmium	516 293 Dy Dysprosium	517 293 Tb Terbium	518 293 Gd Gadolinium	519 293 Eu Europium
521 293 Lu Lutetium	522 293 Yb Ytterbium	523 293 Tm Thulium	524 293 Er Erbium	525 293 Ho Holmium	526 293 Dy Dysprosium	527 293 Tb Terbium	528 293 Gd Gadolinium	529 293 Eu Europium
531 293 Lu Lutetium	532 293 Yb Ytterbium	533 293 Tm Thulium	534 293 Er Erbium	535 293 Ho Holmium	536 293 Dy Dysprosium	537 293 Tb Terbium	538 293 Gd Gadolinium	539 293 Eu Europium
541 293 Lu Lutetium	542 293 Yb Ytterbium	543 293 Tm Thulium	544 293 Er Erbium	545 293 Ho Holmium	546 293 Dy Dysprosium	547 293 Tb Terbium	548 293 Gd Gadolinium	549 293 Eu Europium
551 293 Lu Lutetium	552 293 Yb Ytterbium	553 293 Tm Thulium	554 293 Er Erbium	555 293 Ho Holmium	556 293 Dy Dysprosium	557 293 Tb Terbium	558 293 Gd Gadolinium	559 293 Eu Europium
561 293 Lu Lutetium	562 293 Yb Ytterbium	563 293 Tm Thulium	564 293 Er Erbium	565 293 Ho Holmium	566 293 Dy Dysprosium	567 293 		