

# DETECTION OF FUNCTIONAL GROUPS

## Using Organic Compounds, The Functional Groups are Detected

**Organic chemistry:** - is the study of the structure, properties, composition, reactions, and preparation of carbon-containing compounds, which include not only hydrocarbons but also compounds with any number of other elements, including hydrogen (most compounds contain at least one carbon–hydrogen bond), nitrogen, oxygen, halogens, phosphorus, silicon, and sulfur. This branch of chemistry was originally limited to compounds produced by living organisms but has been broadened to include human-made substances such as plastics. The range of application of organic compounds is enormous and also includes, but is not limited to, pharmaceuticals, petrochemicals, food, explosives, paints, and cosmetics.

## What are Hydrocarbons?

Organic compounds contain only carbon and hydrogen are called Hydrocarbons. Hydrocarbons can be classified into two:

- A- Saturated Hydrocarbons (Alkanes).
- B- Unsaturated Hydrocarbons (Alkenes & Alkynes).

### **A- Saturated Hydrocarbons (Alkanes)**

Hydrocarbons that contain carbon-carbon single bonds are called saturated hydrocarbons. They are also called Paraffins or Aliphatic Hydrocarbons. They may have straight chain, branched or ring structure.

### **B- Unsaturated Hydrocarbons (Alkenes & Alkynes)**

Hydrocarbons that contain carbon-carbon double bond or triple bond are called unsaturated hydrocarbons.

**Functional Groups:** - are small groups of atoms that exhibit a characteristic reactivity. A particular functional group will almost always display its distinctive chemical behavior when it is present in a compound. Because of their importance in understanding organic chemistry, functional groups have specific names that often carry over in the naming of individual compounds incorporating the groups.

As we progress in our study of organic chemistry, it will become extremely important to be able to quickly recognize the most common functional groups, because they are the key structural elements that define how organic molecules react. For now, we will only worry about drawing and recognizing each functional group, as depicted by Lewis and line structures. Much of the remainder of your study of organic chemistry will be taken up with learning about how the different functional groups tend to behave in organic reactions.

Aim: -

Our objective is to identify the functional groups present in an organic compound through;

Tests for Unsaturation

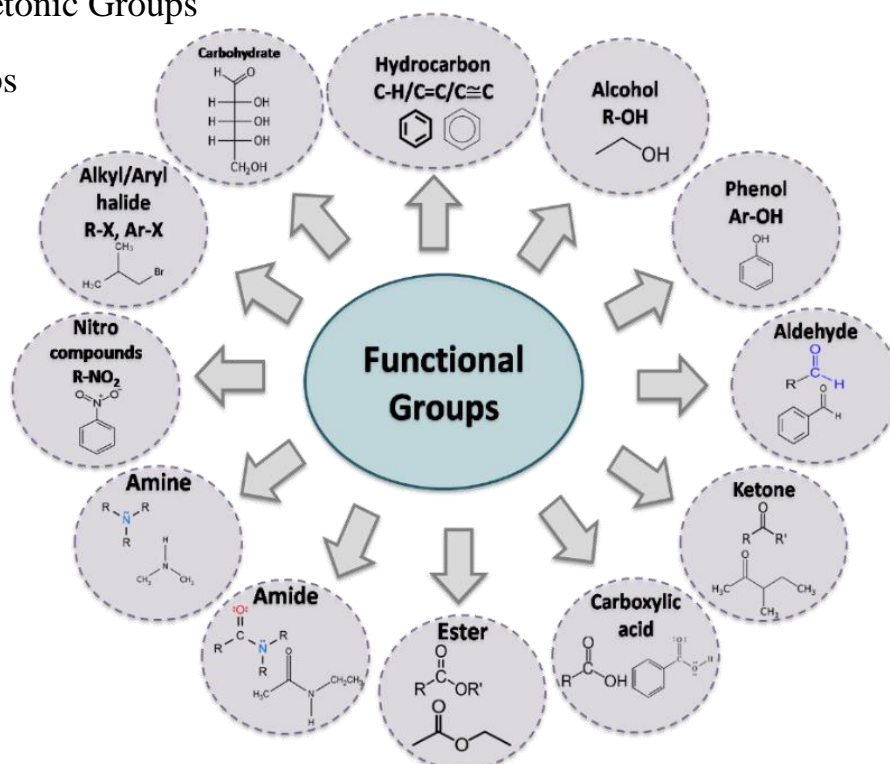
Tests for Alcoholic Group

Tests for Phenolic Group

Tests for Aldehydic and Ketonic Groups

Tests for Carboxylic Groups

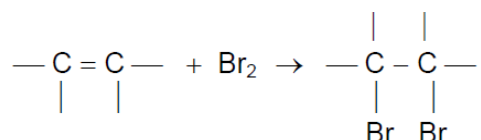
Tests for Amino group



## I. Characteristic reactions differentiating saturated aliphatic hydrocarbons from unsaturated aliphatic hydrocarbons

### 1. The test of bromine addition.

Unsaturated hydrocarbons and other compounds with unsaturated bonds decolorize bromine solution in consequence of addition reaction.

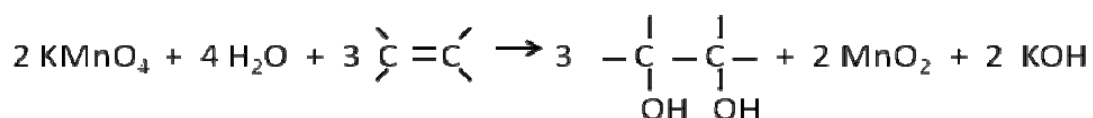


#### Procedure:

Add dropwise 1 % acetic acid solution of bromine to about 0.5 ml of sample dissolved in acetic acid or other organic solvent. Mix carefully the contents of the test tube. The pink color of bromine quickly disappears to the moment, when total multiple bonds are saturated.

### 2. The test with potassium permanganate by Lehman.

The solution of  $\text{KMnO}_4$  submits decolorization in the presence of compounds with unsaturated bonds. This is the consequence of manganese reduction from  $+7$  to  $+2$ . During reaction, the solution becomes alkaline ( $\text{KOH}$  is formed) and the brown precipitate of manganese dioxide can appear in the reaction mixture.



#### Procedure:

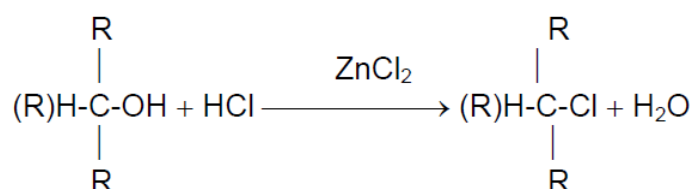
Add dropwise (0.1%) acetone solution of  $\text{KMnO}_4$  to about (1ml) of examined sample. Mix the solution carefully after addition of each drop and wait for disappearance of  $\text{KMnO}_4$  pink color.

The quantity of decolorized solution and the speed of its decolorizing depend on the amount of multiple bonds in the molecule of examined compound.

## II. Characteristic Reactions of Alcohols

### 1. The Lucas test (1 test per group).

Primary, secondary and tertiary alcohols react in different way with Lucas' reagent (the solution of anhydrous zinc chloride in concentrated hydrochloric acid). Primary alcohols, containing less than six carbon atoms, do not react with the reagent, and give clear, slightly dark solution. With secondary alcohols, turbidity of the solution appears, forming two phase solution after 1-1.5 hours. In the presence of tertiary alcohols, the solution turbidity and solution separation for two phases form very quickly. Tertiary alcohols react with concentrated HCl even in the absence of ZnCl<sub>2</sub>.



#### Procedure:

Add 5 ml of Lucas' reagent to three dry test tubes with ground-in stoppers, containing respectively primary, secondary and tertiary alcohols (0.5 ml). Mix the content for a while, put them away to the laboratory rack, and check the time difference, necessary in each case for turbidity and two phase solution formation.

### 2. The test with mercury sulfate (HgSO<sub>4</sub>) for tertiary alcohols by Deniges.

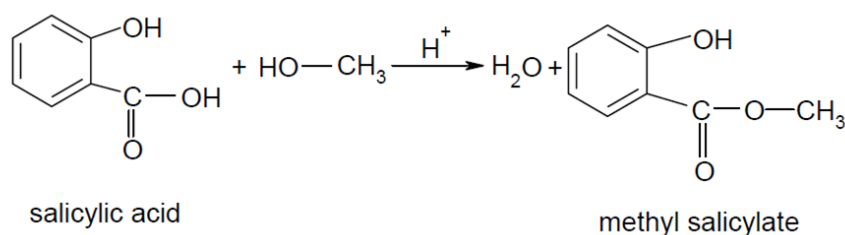
Only tertiary alcohols submit to this reaction. After dehydration, they form unsaturated hydrocarbons. In these conditions, secondary alcohols form only turbid solution and primary ones only opalescence, because of very low speed of alkenes formation.

#### Procedure:

Add 1-2 drops of tertiary alcohol solution to about 1 ml of Deniges reagent (the solution of mercury sulfate in diluted sulfuric acid). Heat the sample in the boiling water bath until a yellow sediment appears.

### 3. The Esterification test – detection of methanol.

Salicylic acid methyl ester (methyl salicylate) is formed by heating of methyl alcohol with salicylic acid in the presence of concentrated sulfuric acid, acting both as a catalyst and a water bonding agent.

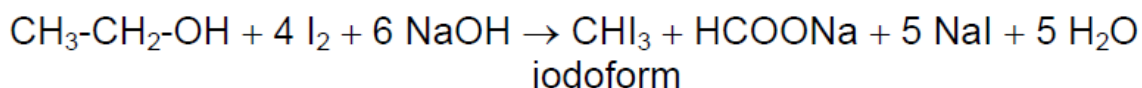


#### Procedure:

Add a pinch of salicylic acid and about 1 ml of concentrated H<sub>2</sub>SO<sub>4</sub> to 1 ml of methanol. After mixing, heat the sample in the boiling water bath. After a few minutes, specific resinous aroma of methyl salicylate will appear.

### 4. The iodoformic test by Lieben – detection of ethanol.

Among primary alcohols, only ethanol undergoes iodination reaction. This is the summarized notation of the reaction:



#### Procedure:

To 0.5ml of ethanol solution add about 1 ml of iodine in potassium iodide solution (Lugol's solution). Then add dropwise (2-4 drops) of 5% NaOH water solution, till yellow color of iodine will disappear. After mixing and heating the tube content to 60°C, specific aroma and yellow crystals of iodoform will appear.

## **5. Reaction of phenol with ferric chloride**

Ferric chloride reacts with the hydroxyl groups of phenols and phenol derivatives and forms stable-colored complexes: violet, violet-bluish, blue, green and red. This reaction depends on the structure and presence of complex-created groups (aldehyde, ketone, carboxylic, hydroxyl, or sulfonic) located in the orto-position of phenols. Phenols without complex-created groups in the orto-position react with  $\text{FeCl}_3$  only in water, forming unstable complex color compounds.

### **Procedure:**

Add 1 drop of 2%  $\text{FeCl}_3$  solution to 1% phenol water solution (3 ml). A violet color of this mixture

will form. The color disappears after addition of some drops of 1 M sulfuric acid.

## **III. Characteristic Reactions of Aldehydes and Ketones**

### **1. Schiff's reagent test - Detection of Aldehydes.**

The Schiff test is a chemical test used to check for the presence of aldehydes in a given analyte. This is done by reacting the analyte with a small quantity of a Schiff reagent (which is the product formed in certain dye formulation reactions such as the reaction between sodium bisulfite and fuchsin).

### **Procedure:**

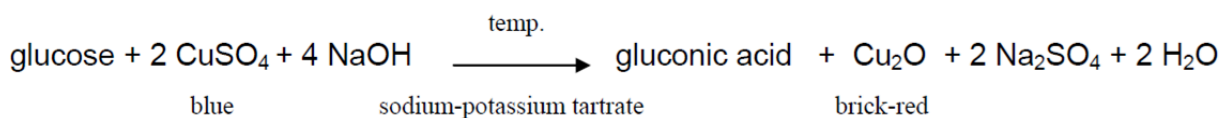
To 2ml of formic aldehyde solution add a few drops of Schiff's reagent (basic fuchsin in sodium meta-bisulfite solution) and mix. After a few minutes, a purple (amaranth) color will appear.

## 2. Reduction tests of Aldehydes

These tests reveal reducing properties of aldehydes and carbohydrates. They are based on the reduction of heavy metal ions and simultaneous oxidation of carbonyl group of aldehydes or monosaccharides to carboxyl group, through the reagent Fehling's I and II.

### Fehling's test

The Fehling reagent is composed of two separate solutions: (Fehling I) is solution of  $\text{CuSO}_4$  in diluted  $\text{H}_2\text{SO}_4$ , and (Fehling II) is sodium potassium tartrate in diluted  $\text{NaOH}$ . In an alkaline milieu, the insoluble blue sediment  $\text{Cu}(\text{OH})_2$  is released, however, in the presence of tartrate it remains in solution in a form of tartrate complex compound:



### Procedure:

In a test tube, mix 1ml of Fehling I reagent and 1 ml of Fehling II. Heat until boiling and then add a few drops of formic solution. Mix well and prolong the heating in water bath. Observe the precipitation of the orange-red colored sediment of cuprous oxide  $\text{Cu}_2\text{O}$ .

#### IV. Characteristic Reactions of Carboxylic Acids

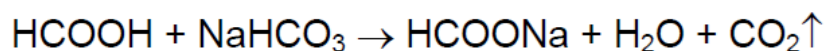
To identify the presence of carboxylic functional group in a given organic compound.

##### 1. Reaction of carboxylic acids with sodium bicarbonate $\text{NaHCO}_3$ .

Carboxylic acids are versatile organic compounds. It has excellent physical and chemical properties. The carboxylic acid chemical structure contains a carbonyl functional group and hydroxyl group. It interacts easily with polar compounds and contributes to many important chemical reactions. The carboxylic acids are the most important functional group that present  $\text{C}=\text{O}$ . Although the carboxylic acids are weaker comparing to mineral acids, but stronger than carbonic acid ( $\text{H}_2\text{CO}_3$ ). Specific reactions of carboxylic acids depend on organic part that is connected to carboxylic group or the presence of additional functional group.

When carboxylic acid reacts with sodium bicarbonate solution carbon dioxide is evolved with a brisk effervescence along with sodium acetate is formed.

**The chemical reaction is given below.**



Note: This test is used to distinguish between carboxylic acid from phenol. Phenol does not answer to this test.

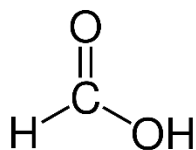
##### **Procedure:**

Add about 1 ml of 5%  $\text{NaHCO}_3$  solution to 1 ml of short-chain carboxylic acid solution (formic acid -  $\text{HCOOH}$ ). After shaking, observe the release of  $\text{CO}_2$  gas bubbles, gathering on the tube walls.

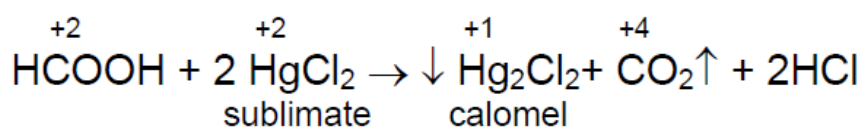


## 2. Formic acid (methanoic acid) detection

Formic acid is the only one, which possesses both carboxyl and aldehyde groups activities:



The reducing property of formic acid cannot be demonstrated using a typical reducing test (in alkaline medium), because of its strong acidic dissociation in water solution. However, its reducing property can be demonstrated in the following reaction:

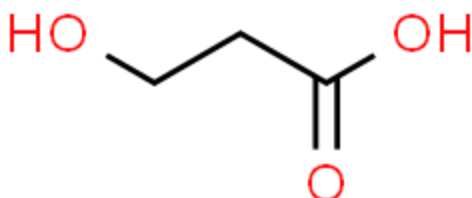


### Procedure:

Add a few drops of 5% mercuric chloride  $\text{HgCl}_2$  (a corrosive sublimate) to (1ml) of formic acid solution. Heat in a water bath to obtain the white precipitate of mercurous chloride (calomel).

## 3. Lactic acid ( $\alpha$ -hydroxypropionic acid) Detection

Lactic acid is an organic acid. It has a molecular formula  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ . It is white in the solid state and it is miscible with water. When in the dissolved state, it forms a colorless solution. Production includes both artificial synthesis as well as natural sources.



Lactic acid is an alpha-hydroxy acid (AHA) due to the presence of a hydroxyl group adjacent to the carboxyl group. It is used as a synthetic intermediate in many organic

synthesis industries and in various biochemical industries. The conjugate base of lactic acid is called lactate.

Organic acids with  $\alpha$ -hydroxyl group change the color of **Uffelmann's reagent** to yellow-greenish.

#### **Procedure:**

Prepare Uffelmann's reagent in test tube by adding 1-3 drops of  $\text{FeCl}_3$  solution to 2 ml 1% solution of phenol (one reagent for all the students). Mix, and add a few drops of the reagent to 1 ml of lactic acid solution. Lactic acid solution changes the violet color of the reagent to light yellow-greenish, and is decolorized by hydrochloric acid.

#### **4. Salicylic Acid Detection**

Salicylic acid (SA), as a major phytohormone, generally plays an important role in regulating diverse physiological processes such as defense responses, thermogenesis. Moreover, Salicylic acid is a promising material and it is commonly exploited in the manufacture of pharmaceutical products. Additionally, SA is widely used in the cosmetics industry as an organic acid, for example, Aspirin, as a widely used drug, has the effects of an antipyretic, analgesic and anti-inflammatory. However, SA can be easily produced due to the incomplete acetylation in the production process of aspirin or hydrolysis during the refining process and storage. Besides, the phenolic hydroxyl group in the free SA is readily oxidized and consequently form a series of colored quinone compounds, leading to discoloration of aspirin. There have corresponding safety limits for free SA in aspirin in countries around the world. From the above consideration, the contents of SA need to be frequently determined to ensure people's health.

Thus, SA has broadened application prospects in many fields. However, SA is one of the common pollutants in industrial wastewater. More importantly, SA may cause some toxic side effects on the human body. Because of its relatively strong acidity, SA can not only stimulate and damage the mouth, esophagus, and gastric membrane, but can also invoke adverse symptoms such as metabolic disorders, ototoxicity, fetal malformations, and central nervous system depression.

**Procedure:**

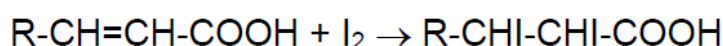
Add to test tube 1 ml of water, a few crystals of salicylic acid and 1 drop of FeCl<sub>3</sub> solution. Observe the violet color, similar to previously performed FeCl<sub>3</sub> reaction with phenol solution.

**5. Detection of Unsaturated Fatty Acids**

Fatty acids are high-calorie fatty acids made up of a hydrogen-surrounded carbon chain. The reason for the description of these fats with acidity is that one end of the carbon chain ends with the acid part COOH. While the other ends with a carbon atom attached to three hydrogen atoms. Nitroalkene fatty acids are unsaturated fatty acids that contain a nitro group adjacent to a double bond. They can be formed endogenously through the initial addition of nitrogen dioxide (NO<sub>2</sub>) to an unsaturated fatty acid. Nitrogen dioxide originates from nitrite (NO<sub>2</sub><sup>-</sup>) under acidic conditions, from nitric oxide (NO·) autooxidation, from peroxynitrite (ONOO<sup>-</sup>) decay or from peroxidase-mediated nitrite oxidation. Thus, the nitration of fatty acids is favored in the contexts of digestion and inflammation. The molecular pathways leading to nitroalkene fatty acid. Although several synthetic drugs such as sulfonylureas, biguanides, alpha-glucosidase inhibitors and others are currently being used for the treatment of diabetes mellitus (T2DM), some of them have been associated with adverse effects such as hypoglycemia, liver damage, gastrointestinal symptoms, and weight gain.

**A. Addition Reaction with Iodine Solution**

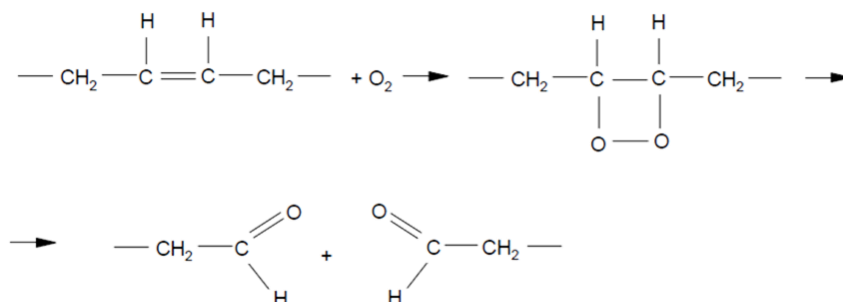
Unsaturated fatty acids react with iodine (and other halogens) discoloring the iodine solution and yielding iodine addition products.

**Procedure:**

Add a few drops of Hüble's reagent (iodine in alcoholic solution of HgCl<sub>2</sub>) to 1 ml of olive oil (oleic acid), and shake. After a few minutes the solution becomes colorless.

## B. Oxidation Reaction

Double bonding in unsaturated fatty acids is sensitive to oxidation. In the presence of oxidizing reagents (also oxygen and its free radicals) the molecule of unsaturated fatty acid, in the place where double bonding exists, is broken into two molecules of aldehyde. This process can be observed after a few days' exposition of fat to open air and sunlight (rancid process).

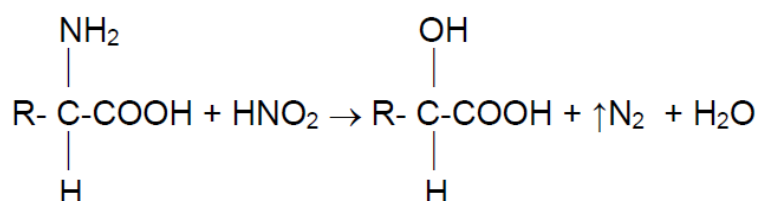


### Procedure:

Add 3 drops of olive oil to 1 ml of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) solution and then a few drops of potassium permanganate solution ( $\text{KMnO}_4$ ), and mix. After a few minutes, the permanganate solution becomes colorless.

## V. Characteristic Reaction of Aliphatic Amines

The primary amino group, present on alpha carbon atom of each amino acid, reacts with nitrous acid producing alpha-hydroxy acid, nitrogen gas and water.



### Procedure:

Dissolve a small amount of sodium nitrite salt ( $\text{NaNO}_2$ ) in 1 ml of 2M sulfuric acid solution.

Observe slow bubbling of released nitric oxide gas. Then, in a hood compartment, add to the tube a few drops of amino acid (glycine) solution. Observe a massive bubbling of nitrogen gas, forming gas bubbles settled on the tube walls.

## Chemical Calculations for Preparing Solutions for Detection of Functional Groups

- Divided into two parts:-

- A. Liquid solutions
- B. Solid solutions

### ❖ **Molarity (M)**

Molar concentration or molarity is most commonly expressed in units of moles of solute per litre of solution. For use in broader applications, it is defined as amount of substance of solute per unit volume of solution, or per unit volume available to the species or a molar solution is a solution of which one liter contains one gram molecular weight of the solute in the form of molecules or ions, represented by lowercase (M)

### ❖ **Equivalent concentration (Normality (N))**

Normality is a measure of concentration equal to the gram equivalent weight per litre of solution. Gram equivalent weight is the measure of the reactive capacity of a molecule. The solute's role in the reaction determines the solution's normality. Normality is also known as the equivalent concentration of a solution. In chemistry, the equivalent concentration or normality of a solution is defined as the molar concentration divided by an equivalence factor.

**Normality (N) use (eq.wt)**

Calculations for Molarity (M) and Normality (N)

**Molarity (M) use (M.Wt)**

**Normality (N) use (Eq.Wt)**

**A. Liquid solutions**

$$N1 = \frac{SP. * Wt.\% * 1000}{Eq. Wt.} \text{ ----- (1)}$$

Where:-

N1 = For example, sulfuric, hydrochloric, or nitric acid, etc., are concentrated or diluted liquid solutions calibration Centre

Sp. = Specific weight of acid (acid density)

Wt. % = The percentage of the weight of Liquid solutions

$$N_1 * V_1 = N_2 * V_2 \text{ ----- (2)}$$

$$V1 = \frac{N2 * V2}{N1} \text{ ----- (3)}$$

## B. Solid solutions or Liquid solutions

To calculate the weight of (Solid solutions) necessary preparation solution (0.1N) using the following equation:

$$N = \frac{W_t}{\text{Eq.Wt}} * \frac{1000}{V} \text{ ----- } 4$$

$$W_t = \frac{N * V * \text{Eq.Wt}}{1000} \text{ ----- } 5$$

Where:

Wt = weight of sodium carbonate, which is dissolved in a given volume of water

N = calibration solution of Solid solutions to be preparing = 0.1

V = volume of the solution to be prepared (ml)

Eq.Wt = equivalent weight of Solid solutions