*Republic of Iraq*

*Ministry 0f Higher Education and scientific Research*

*Al-Mustansiriya University*

*Collage of Science*

*Department of Chemistry*

# *Practice Volumetric Chemical Analysis*

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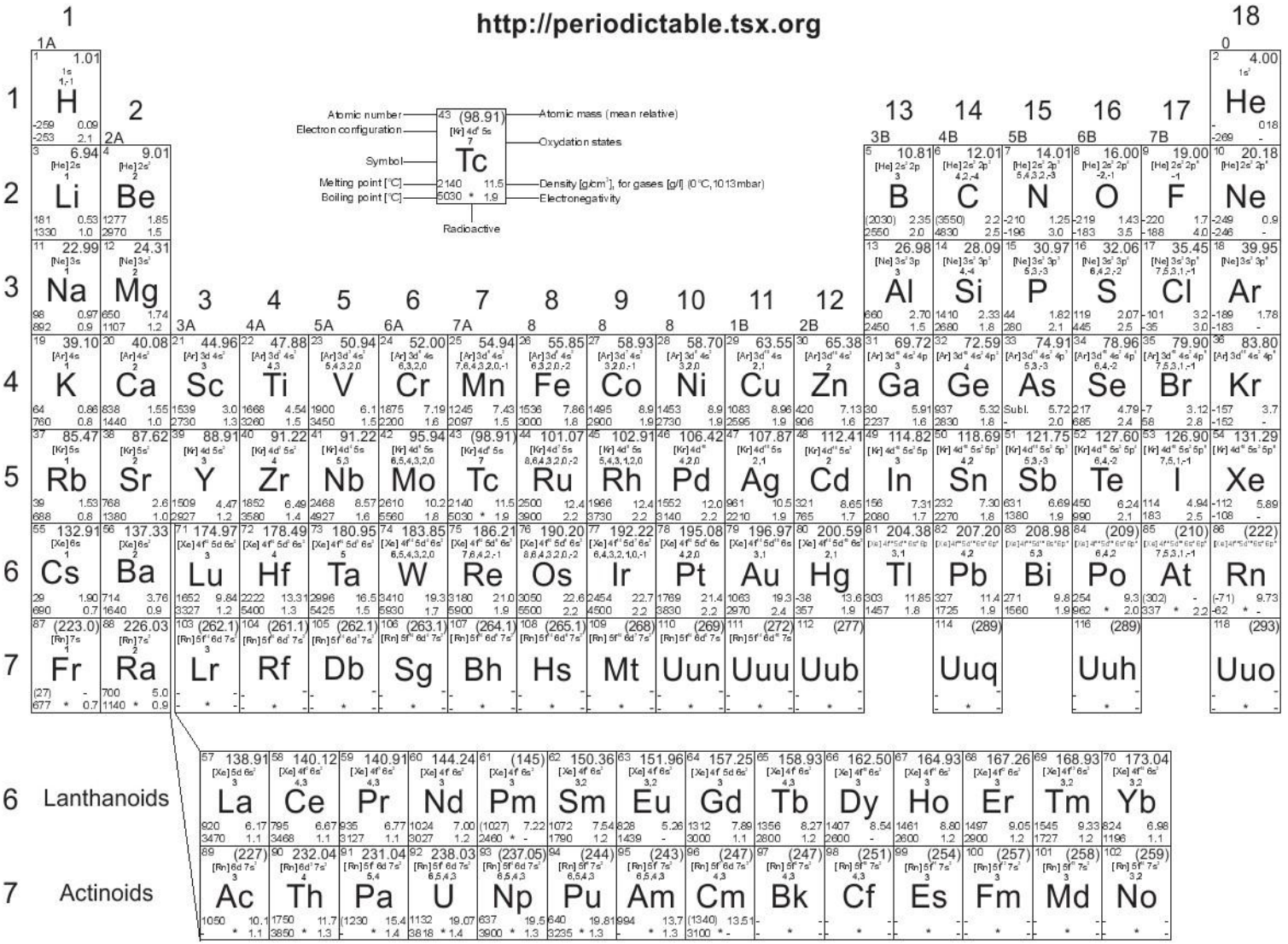
# ChemGlobe - Periodic table of elements

http://periodictable.tsx.org



## Rules for the handing of reagents and solutions:-

1. Select the best available grade of chemical for analytical work.

2. Replace the top of every container immediately after the removal of reagent, do not rely on someone else to do this.

3. Hold stoppers of reagent bottles between the fingers, stoppers should never be set on the desk top.

4. Unless specifically directed to the country, never return any excess reagent or solution to a bottle. The minor saving represented by the return of an excess is overshadowed by the risk of contaminating the entire bottle.

5. Again, unless specifically directed otherwise, do not insert spoons, spatulas, or knives into a bottle containing a solid chemical. Instead, shake the capped these are used wherever possible in analytical work. Some suppliers label their products with the maximum limits of impurity allowed by these specifications, other print the actual results of analyses for the various impurities.

## Quantitative Analysis:-

The quantitative chemical analysis is a scientific method to determine the absolute or relative abundance of a chemical substance in a sample.

## Volumetric Analysis (titrimetric analysis):-

Chemical procedure used for determining the concentration of a gas (evaluated or consumed) in some reactions and solution by measured of it is volume A known volume of a solution of unknown concentration is reacted with a known volume of a solution of known concentration (**standard solution**). The standard solution is delivered not usually from a burette so the volume added is known. This technique is known as titration. Often an indicator is used to show when the correct proportions have reacted.

The term 'titrimetric analysis' refers to quantitative chemical analysis carried out by determining the volume of a solution of accurately known concentration which is required to react quantitatively with a measured volume of a solution of the substance to be determined. The solution of accurately known strength is called the **standard solution**, see Section 10.3. The weight of the substance to be determined is calculated from the volume of the standard solution used and the chemical equation and relative molecular masses of the reacting compounds.

The term 'volumetric analysis' was formerly used for this form of quantitative determination but it has now been replaced by **titrimetric analysis**. It is considered that the latter expresses the process of titration rather better, and the former is likely to be confused with measurements of volumes, such as those involving gases. In titrimetric analysis the reagent of known concentration is called the **titrant** and the substance being titrated is termed the **titrand**. The alternative name has not been extended to apparatus used in the various operations; so the terms volumetric glassware and volumetric flasks are still common, but it is better to employ the expressions graduated glassware and graduated flasks and these are used throughout this book.

The standard solution is usually added from a long graduated tube called a burette. The process of adding the standard solution until the reaction is just complete is termed a **titration**, and the substance to be determined is **titrated**. The point at which this occurs is called the **equivalence point** or the **theoretical** (or **stoichiometric**) **end point**. The completion of the titration is detected by some physical change, produced by the standard solution itself (e.g. the faint pink colour formed by potassium permanganate) or, more usually, by the addition of an auxiliary reagent, known as an indicator; alternatively some other physical measurement may be used. After the reaction between the substance and the standard solution is practically complete, the indicator should give a clear visual change (either a colour change or the formation of turbidity) in the liquid being titrated. The point at which this occurs is called the **end point of the titration**. In the ideal titration the visible end point will coincide with the stoichiometric or theoretical end point. In practice, however, a very small difference usually occurs; this represents the titration error. The indicator and the experimental conditions should be so selected that the difference between the visible end point and the equivalence point is as small as possible.

mmol standard solution = mmol unknown solution

$$M_1 * V_1 = M_2 * V_2$$

$$M1 * V1 = \frac{Wt.}{M.Wt.} * 1000$$

meq standard solution = meq unknown solution

$$N_1 * V_1 = N_2 * V_2$$

$$N1 * V1 = \frac{Wt.}{Eq.Wt} * 1000$$

## Primary standard solutions:-

Primary standard solutions are used in analytical chemistry. Including dissolving, a primary standard is typically a reagent which can be weighed easily, and which is so pure that its weight is truly representative of the number of moles of substance contained. Features of a primary standard include:

1. High purity (more than 99.98%)
2. They have known formula and molecular weight
3. They are non-sensitive to atmospheric oxygen
4. High Stability (low reactivity for temperature, light, and dust)
5. High solubility (if used in titration)
6. High equivalent weight
7. Non-toxicity
8. Ready and cheap available
9. Should have high molecular weight for weighing errors are minimized

## Secondary standard solutions:-

Secondary standard solutions are a solution that is not stable in its own form, and must first be standardized before being used. A good example of this is NaOH, sodium hydroxide is a secondary standard because it absorbs the moisture from the air than react with $CO_2$ in air to form $Na_2CO_3$ and its concentration wills changes. Features of

Secondary standards include: Influenced by atmosphere/environment

1. Concentration change over time
2. Usually powerful reactants
3. Usually cheap & easy to use
4.

## 1//Acid–base titration:-It is acid react with base to obtain salt and water:-

$$\text{Acid + Base} \rightleftharpoons \text{Salt + Water}$$

An acid-base titration is the determination of the concentration of an acid or base by exactly neutralizing the acid/base with an acid or base of known concentration. This allows for quantitative analysis of the concentration of an unknown acid or base solution. We must be chosen a suitable indicator , the equivalence point of the reaction, the point at which equivalent amounts of the reactants have reacted. The point at which the indicator changes color is called the end point.

| | | Indicator color | |
|---|---|---|---|
| ***Indicator*** | ***pH*** | ***Acidity medium*** | ***Basics medium*** |
| Methyl orange (M.O) | 3.1 – 4.4 | Red | Yellow |
| Bromocresol Green | 3.3 – 4.5 | Yellow | Blue |
| Methyl Red (M.R) | 4.2 – 6.3 | Red | Yellow |
| Bromo Thymol Blue | 6 – 7.6 | Yellow | Blue |
| Phenol Red (P.O) | 6 - 8 | Yellow | Red |
| Cresol Indigo | 7.4 - 9 | Yellow | purple |
| Phenol Phthalin (Ph. Ph) | 8 – 9.8 | Colorless | Red |
| Thymol Blue | 8 – 9.8 | Yellow | Blue |

## Experiment No.(1):- Preparation and standardization of 0.1 M(HCl) hydrochloric acid solution

**Theory:-** Hydrochloric acid is produced in solutions up to 38% HCl (concentrated grade). Higher concentrations up to just over 40% are chemically possible, but the evaporation rate is then so high that storage and handling need extra precautions, such as pressure and low temperature. Laboratory grade hydrochloric acid is not sufficiently pure to be used as a primary standard, because it evaporates easily. In this experiment, a standard solution of sodium carbonate is used to determine the exact concentration of a hydrochloric acid solution. The neutralization reaction that occurs is as follows:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$

Methyl orange indicator solution is used. At the end-point – when neutralization just occurs – the indicator changes color from yellow to peach-pink.

**Procedure:-**

1. **Preparing (50 ml) 0.1 M HCl Solution**:38 % HCL shows density 1.19 g/mL and we can find M by next : -

$$M = \frac{sp.gr * \% * 1000}{M.wt}$$

**Calculate the volume of HCl (conc.)**:- We must dilute it to preparing 0.1 M HCl in 50 ml from next:

$$(M^* V)_{conc.} = (M * V)_{dilute}$$

$$M * V_{ml} = 0.1 * 50_{ml}$$

Transfer V ml by cylinder to clean and dry beaker containing 30 ml D.W, transfer the solution to volumetric flask capacity 50 ml, and complete the volume to the mark by D.W.

2. **Preparing (50 ml) 0.1 M $Na_2CO_3$ Solution**:-calculate amount from sodium carbonate for prepare 0.1 M in 50 ml -

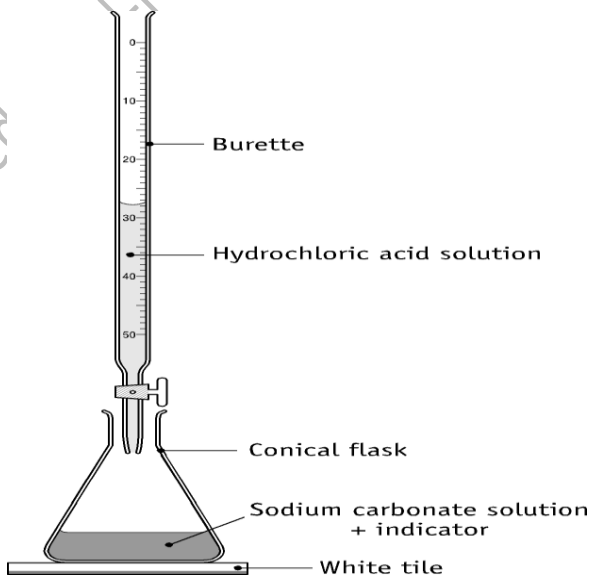
$$M = \frac{Wt.(gm)}{M.Wt.} * \frac{1000}{V(ml)}$$

$$0.1 = \frac{Wt.(gm)}{106} * \frac{1000}{50}$$

$$Wt. = 0.53\ gm$$

Weigh 0.53 gm. from $Na_2CO_3$ in clean and dry beaker and dilute in 30 ml D.W, transfer solution to volumetric flask capacity 50 ml and complete the volume to the mark by D.W.

3. Transfer known volume of 5 ml the sodium carbonate solution, with a pipette, to a conical flask then add one or two drops of methyl orange to this solution.




4. Add the acid unknown solution from the burette gradually with continuous swirling of the solution in the conical flask and near the end point, the acid is added drop by drop. Continue the addition of the acid until the color of the solution passes from yellow to faint red.

5. Repeat the experiment three times and tabulate your results then take the mean of the three readings.

**Calculations:** Calculate the molarity of HCl:-

$$m\ mol\ HCl = m\ mol\ Na_2CO_3$$

$$(M * V)\ HCl = (M * V)\ Na_2CO_3 * \frac{1}{2}$$

$$(M * V_{burette}) = (0.1 * 5) * \frac{1}{2}$$

**Discussion:-**

1. What the difference between primary and secondary standard substances?

2. Calculate the volume of conc. HCl required for preparing 250 ml 0.1 M?

3. Calculate the weight of $Na_2CO_3$ required for preparing 100 ml 0.1 M?

4. Why is sodium carbonate primary solution?

5. Why standard solution should be colorless?

6. Why is HCl not primary solution?

7. What is the titration?

## Experiment No.(2):- Preparation and standardization of 0.1 N sodium hydroxide solution using Direct Titration

**Theory**:- **Potassium hydrogen phthalate**, often called simply **KHP**, is an acidic salt

Compound. It forms white powder, colorless crystals; it is solid and air-stable, making it easy to weigh accurately. KHP is a useful standard for NaOH and Total Organic Carbon (TOC) testing. Most TOC analyzers are based on the oxidation of organics to carbon dioxide and water, with subsequent quantization of the carbon dioxide.

This experiment demonstrates the most common method for obtaining standard solutions for titrimetric analysis. It involves preparation of a solution that has the Approximate concentration desired determination of the concentration by direct **titration** against a **primary standard**. We will standardize the 0.1 N NaOH solution (the titrant) with potassium hydrogen phthalate (KHP, $KC_8H_4O_4H$) using phenolphthalein as the indicator. KHP is a weak acid and reacts with base in the following way:-

$$C_8H_4O_4H^- + OH^- \longrightarrow C_8H_4O_4^{-2} + H_2O$$

**Procedure:-**

1. Preparation (50 ml)0.1N KHP:-

$$N = \frac{\text{Wt.(gm)}}{\text{Eq.wt.}} * \frac{1000}{\text{V(ml)}}$$

$$\text{Wt.} = N * \text{Eq.Wt} * 0.05$$

$$= 0.1 * 204 * 0.05$$

$$= 1.02 \text{ gm}$$

Weigh 1.02 gm from KHP and dilute in 30 ml D.W, transfer solution to volumetric flask capacity 50 ml and complete the volume to the mark by D.W.

2. Preparation (50 ml) 0.1 N NaOH :-

$$N = \frac{\text{Wt.(gm)}}{\text{Eq.wt.}} * \frac{1000}{\text{V(ml)}}$$

$$\text{Wt.} = N * \text{Eq.Wt} * 0.05$$
$$= 0.1 * 40 * 0.05$$
$$= 0.2 \text{ gm}$$

Weigh 0.2 gm from NaOH and dilute in 30 ml D.W, transfer solution to volumetric flask capacity 50 ml and complete the volume to the mark by D.W.

3. Transfer 5 ml volume of the sodium hydroxide solution, with a pipette, to a conical flask then adds one or two drops of phenolphthaline. The solution has the pink color

4. Add the (0.1 N KHP) from the burette gradually with continuous swirling of the solution in the conical flask, and near the end point, the KHP is added drop by drop. Continue the addition of the KHP until the color of the solution discharged.

5. Repeat the experiment three times and tabulate your results then take the mean of the three readings.

**Calculations:**-Calculate the normality and % of NaOH:-

$$\text{meq. NaOH} = \text{meq KHP}$$

$$(N * V)_{NaOH} = (N * V)_{KHP}$$

$$\frac{\text{Wt.}}{\text{Eq.Wt}} * 1000 = (N * V)_{KHP}$$

$$\frac{\text{Wt.}}{40} * 1000 = 0.1 * \frac{V_1 * V_2 * V_3}{3}$$

$$\% \text{ NaOH} = \frac{\text{Wt.}}{\text{Wt. of sample}} * 100$$

**Discussion:-**

**1.** Give 3 reasons why NaOH is not used as a primary standard?
**2.** Calculate ppm and ppt of KHP in this experiment?
**3.** Why is KHP used as a primary standard?
**4.** Why NaOH percentage less than 100%?
**5.** Why used ph.ph indicator?

## Experiment No (3):- Determination of Acetic Acid Content of Vinegar

**Theory:-** Determination of acetic acid concentration in commercially available white vinegar is one of the simplest and easiest titrations. It is also possible to determine concentration of acetic acid in other types of vinegar. The only problem is that the color of the vinegar can make it difficult to spot the end point. However, in most cases even vinegars made of red wine - after being diluted for titration - are pale enough so that the phenolphthalein color at the end point can be easily spotted.

Vinegar can have different strengths. Most popular are concentrations between 4% and 15% In case of such concentrated solutions it may be impossible to simply take a single sample for titration. We won't be able to measure such a volume of liquid with reasonable accuracy, thus we are forced to dilute the original acid.

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

**Colorless** **Red**

Acetic acid reacts with NaOH on the 1:1 basis

**Procedure**:-

1. Weigh accurately 5 ml volume of the Vinegar solution
2. Transfer to 300 ml conical flask and add 50 ml water free from $CO_2$.
3. Add one or two drops of ph. ph. indicator to this solution.
4. Add 0.1 N NaOH from the burette gradually with continuous swirling of the solution in the conical flask and near the end point, NaOH is added drop by drop. Continue the addition of NaOH until the color of the solution passes from Colorless to faint red /pink.
5. Repeat the experiment three times and tabulate your results then take the mean of the three readings

**Calculations:-** Calculate the rate of weighted percentages for Vinegar:-

$$\text{m mol NaOH} = \text{m mol } CH_3COOH * \frac{\text{mole NaOH}}{\text{mole } CH_3COOH}$$

$$(M * V_{burette})_{NaOH} = \frac{Wt.}{M.Wt} * 1000 * \frac{1}{1}$$

$$(M * V)_{NaOH} = 1000 * \frac{Wt.\ CH_3COOH}{60.05}$$

$$\frac{Wt.}{Wt.}\%\ CH_3COOH \text{ in vinegar} = \frac{Wt.\ CH_3COOH}{Wt.\ of\ vinegar} * 100$$

$$\frac{Wt.}{V}\%\ CH_3COOH \text{ in vingar} = \frac{Wt.\ CH_3COOH}{V\ of\ sample\ (vingar)} * 100$$

**Discussion**:-

1. A word equation summarizing the souring of wine is:

Grain alcohol ($C_2H_5OH$) + oxygen → acetic acid + water.

Please convert this word equation to a balanced chemical equation.

2. Different vinegars may have different percentages of acetic acid. Is vinegar a mixture, compound, or an element?

3. There are two kinds of vinegars, what the different between them?

## Experiment No.(4):-Determination of acids in wines

**Theory:-**Acids are present in wine in many forms, but the largest percentage of acidity comes from three primary types of acid: Tartaric acid, Malic acid, Citric acid. The chart below provides guidelines for acidity based on the type of wine you are making. Individual tastes vary, of course, so the information shown are recommendations only:-

| Wine Style | Recommended Acidity Range |
|---|---|
| Dry White Wine | 0.65 % - 0.75 % |
| Sweet White Wine | 0.70 % - 0.85 % |
| Dry Red Wine | 0.60 % - 0.70 % |
| Sweet Red Wine | 0.65 % - 0.80 % |
| Sherry Grape Wines | 0.50 % - 0.60 % |
| Non-grape White Wines | 0.55 % - 0.65 % |
| Non-grape Red Wines | 0.50 % - 0.60 % |

**Procedure:-**

**1.** Pipette 50 ml from wines into 250 ml conical flask

**2.** Add 50 ml of D.W

**3.** Add 2 drops of Ph.Ph. indicator.

**4.** Titrate with standard 0.1 N NaOH till the color change to pink

**Calculation**: Express the acidity of the wines as percent (w/v) tartaric acid $C_2H_4O_2$ $(COOH)_2$ (fw=150.09):-

$$\text{m eq NaOH} = \text{m eq tartaric acid}$$

$$(N * V_{\text{burette}})_{\text{NaOH}} = \frac{\text{Wt.}}{\text{Eq. Wt.}} * 1000$$

$$0.1 * V = \frac{\text{Wt.}}{\text{Eq. Wt.}} * 1000$$

$$\frac{\text{Wt. \%}}{V} = \frac{\text{Wt. tartaric acid}}{\text{V of wines}} * 100$$

**Discussion**:-

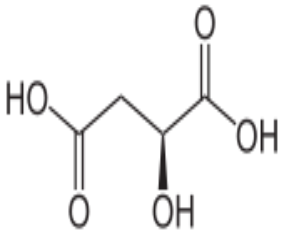
**1.** What is the formula of tartaric acid, malic acid and citric acid?

**2.** What are the primary types of acid in wines?

**3.** Why choice the ph.ph indicator?

## Experiment No.(5):- Determination of Malic acid in Tomatoes

***Theory:-*** The type of acid is found in tomato sauce is mostly Citric acid and Malic acid at a 1 to 0.6 ratio respectively in the ripe red fruit. In the green fruit the ratio is 1 to 1.3 Malic acid is an organic compound with the formula $HO_2CCH_2CHOHCO_2H$. It is a dicarboxylic acid which is made by all living organisms, contributes to the pleasantly sour taste of fruits, and is used as a food additive.




**Procedure:-**

**1.** Use a clean and dry safety pipette. Draw up 10 ml of tomato sauce and discharge it into a 50 ml volumetric flask, and complete the volume to the mark with D.W.

**2.** Transfer the solution to the conical flask, Add 3 drops of phenolphthalein indicator.

**3.** Titrate with standard 0.1 N NaOH until the color changes from colorless to pink
**Calculation**: Express the acidity of the tomatoes sauce as percent (w/v) Malic acid $\mathbf{C_4H_6O_5}$ (fw= 134.09):-

$$\text{m eq NaOH} = \text{m eq malic acid}$$

$$(N * V_{\text{burette}})_{\text{NaOH}} = \frac{\text{Wt.}}{\text{Eq. Wt.}} * 1000$$

$$0.1 * V = \frac{\text{Wt.}}{\text{Eq.Wt.}} * 1000$$

$$\frac{\text{Wt. \%}}{\text{V}} = \frac{\text{Wt. malic acid}}{\text{V of tomato sause}} * 100 = \frac{\text{Wt.}}{10} * 100$$

**Discussion**:-

1. What type of acid is found in tomato sauce?
2. What is the formula of Malic acid?
3. What is the deference between malic acid and acetic, sulfuric acid?

## Experiment No.(6):- Determination of Ammonia in Ammonium salt

**Theory:-** Ammonia is a very toxic gas, what you buy in the store as "ammonia" is a very dilute solution of ammonia in water. When dissolved in water, it forms a very alkaline solution (it is actually ammonium hydroxide, $NH_4OH$) that is an excellent solvent for non-polar molecules like oils.

Two methods: 1. the direct method, a solution of the ammonium salt is treated with a solution of a strong base (NaOH) and the mixture distilled. Ammonia is quantitativty expelled, and is absorbed in an excess of standard acid (HCl).

$$NH_4^+ + NaOH \longrightarrow NH_4OH + Na^+$$

$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$$

2. Indirect method, a solution of the ammonium salt is treated with formaldehyde to prepare hexa amine compound

$$NH_4Cl + 6HCHO \longrightarrow (CH_2)_6N_4 + HCl$$

hexa amine compound is weak base titrate with standard solution is NaOH.

**Procedure:-**

1. Weigh accurately 1 gm from ammonium chloride.

2. Dissolve salt in 100 ml D.W and transfer to conical flask capacity 200 ml, and complete the volume to the mark.

3. Transfer 5 ml from solution, with a pipette, to a conical flask. Capacity 300 ml.

4. Add 25 ml from D.W with a pipette.

5. Add 3 -4 drops from ph.ph indicator, and titrate the solution against (0.1 N NaOH), till the color change to pink.

6. Repeat the experiment three times and tabulate your results then take the mean of the three readings.

**Calculations:-**Calculate the normality and % of ammonium chloride:-

$$(N * V)_{NaOH} = (N * V)_{NH_4Cl}$$

$$(N * V)_{NaOH} = \frac{Wt.}{Eq.wt} * 1000$$

$$(0.1 * V) = \frac{Wt.}{34} * 1000$$

$$\frac{Wt.}{Wt.} \% NH_3 = \frac{Wt.}{Wt.\ of\ sample} * 100$$

**Discussion**:-

1. What is Ammonia?
2. What is hexa amine compound?
3. What is the different between ammonia and ammonium hydroxide?

## Experiment No.(7):- Determination of the relative molecular mass of an organic acid

**Theory**:- Many of the common carboxylic acids are readily soluble in water and can be titrated with sodium hydroxide or potassium hydroxide solutions. For sparingly soluble organic acids the necessary solution can be achieved by using a mixture of ethanol and water as solvent. But for determinations carried out in aqueous solutions it is not normally possible to differentiate easily between the end points for the individual carboxylic acid groups in diprotic acids, such as succinic acid, as the dissociation constants are too close together. In these cases the end points for titrations with sodium

hydroxide correspond to neutralization of all the acidic groups. As some organic acids can be obtained in very high states of purity, sufficiently sharp end points can be obtained to justify their use as standards,e.g. benzoic acid and succinic acid.

The titration procedure described in this section can be used to determine the relative molecular mass (R.M.M.) of a pure carboxylic acid (if the number of acidic groups is known) or the purity of an acid of known R.M.M.

**Procedure**:-

1. Weigh out accurately about 4 g of the pure organic acid, dissolve it in the minimum volume of water (Note 1), or 1:1 (v/v) ethanol/water mixture, and transfer the solution to a 250 mL graduated flask.

2. Ensure the solution is homogeneous and make up to the required volume. Use a pipette to measure out accurately a 25 mL aliquot and transfer to a 250 mL conical flask.

3. Using two drops of phenolphthalein solution as indicator titrate with standard 0.2M (approx.) sodium hydroxide solution (Note 2) until the colorless solution becomes faintly pink.

4. Repeat with further 25 mL volumes of the acid solution until two results in agreement are obtained.

**Calculation**:- The relative molecular mass is given by:

$$R.M.M = \frac{1000\ W * P}{10\ V * M}$$

Where:-

W= is the weight of the acid taken,

P= is the number of carboxylic acid groups,

M= is the molarity of the sodium hydroxide.

V= is the volume of sodium hydroxide used, and

****Notes. (1) In order to obtain sharp end points all de-ionized water used should be carbon-dioxide-free, as far as is possible.**

**(2) Volumes of 0.2M sodium hydroxide required will normally be in the range from about 15 mL to 30 mL depending upon the nature of the organic acid being determined**.

**Discussion**:-

1. What is the difference between R.M.M and molecular weight?
2. Why does the titration taken in (1:1) ethanol: water medium?
3. Write equation to express this titration?

## Experiment No.(8):- Determination of the equivalent weight of a weak acid

**Theory:-**The equivalent weight of an acid, which is an aid in establishing it is identity, is readily determined by titrating a weighed quantity of the purified acid with standard sodium hydroxide.

**Procedure:-**

**1.** Weigh 0.1 mg individual samples into 250 ml conical flask.

**2.** Dissolve in 50-75 ml D.W (see note).

**3.** Add 2 drops of ph.ph indicator.

**4.** Titrate with standard base to the first persistent (30 sec.) color of the indicator.

**Calculation:-**Calculate the equivalent weight of the acid:-

$$\text{Eq. Wt. of acid} = \frac{\text{M.Wt of acid}}{\text{no. of proton } (H^+)}$$

****note: acids with limited solubility in water may dissolve more readily in ethanol or an ethanol-water mixture. The alcohol may be measurably acidic and should be rendered faintly alkaline to ph.ph before it is used as a solvent. As excess of standard base, the excess being determined by back-titration with standard acid.**

**Discussion**:-

1. The weight of $H_2C_2O_4$ is 0.5 gm dissolved in 100 ml D.W, what the normality of $H_2C_2O_4$?
2. What are the Eq. Wt of acetic acid, $H_2SO_4$, oxalic acid and $H_3PO_4$?
3. What are the Eq. Wt. of malic acid, tartaric acid and arsenic acid?

# Experiment No.(9):- Back titration

**Theory:-** Direct titration involves the direct and stepwise addition of a standard titrant to the analyte whilst the back titration involves reacting a standard excess titrant with an analyte solution of an unknown concentration, then reacting the excess (left over) titrant with an analyte of known concentration to determine the concentration of excess titrant.

While In back titration we use two reagents (standard solution) - one, that reacts with the original sample (let's call it A, first standard solution ), and second (lets call it B , second standard solution), that reacts with the first reagent, We add precisely measured amount of reagent A to sample and once the reaction ends we titrate excess reagent A left with reagent B. Knowing initial amount of reagent A and amount that was left after the reaction (from titration) we can easily calculate how much reagent A was used for the first reaction. In this test, we want to find normality for nitric acid, so we added excess amount from NaOH , and the excess amount from NaOH back titration with standard solution like HCl.

$$HNO_3 + NaOH \longrightarrow NaNO_3 + H_2O + NaOH_{excess}$$

$$NaOH_{excess} + HCl \xrightarrow{ph.ph} NaCl + H_2O$$

pink → colorless

**Procedure:-**

1. Transfer 5 ml volume of the nitric acid solution to a conical flask.

2. Transfer 7 ml volume of the 0.1 N NaOH solutions to the same conical flask.

3. Add one or two drops of ph.ph to this solution and complete the titration with (0.1 N HCl) comes from the burette until the color change from pink to colorless.

4. Repeat the experiment three times and tabulate your results then take the mean of the three readings.

**Calculations:-**Calculate the normality of nitric acid:-

$$(N * V)_{HNO3} = (N * V)_{NaOH} - (N * V)_{HCl}$$

$$(N * 5) = (0.1 * 7) - \left[ (0.1 * \frac{(V1 * V2 * V3)}{3} \right]$$

**Discussion:-**1. What difference between HCl and $HNO_3$?

1. How does back titration differ from a direct titration?

2. Why is a back titration sometimes used for an analysis rather than a direct titration?

## Experiment No.(10):- Determination of $Na_2CO_3$ content of washing soda

**Theory:-**Chemically, washing soda is known as sodium carbonate. It is also often referred to as soda ash or soda crystals. Washing soda is a sodium salt and is obtained from carbonic acid. It is widely available in the form of a white powder. It is mostly found in a crystalline form as a heptahydrate (where each sodium carbonate molecule is bonded with seven molecules of water). On exposure to air, it loses the water molecules to form a monohydrate. When it dissolves in water, its molecules break down and ions of sodium and carbonate are released. Washing soda is a key component of laundry soaps and other household cleaning products as it can easily remove dirt and tough greasy stains from clothes, utensils, floors, and various other surfaces. It is also used as a cleansing agent for removing dirt stuck on silver and glass items. When it is dissolved in water, the solution acts as a fungicide that can kill mold and mildew in the damp areas of the house. Water in the swimming pools turns acidic due to repeated addition of chlorine as a disinfectant. Washing soda is added to this water to make it chemically neutral.

**Procedure:-**

**1.** Weigh out accurately about 3.6 g of the washing-soda crystals, dissolve in water, and make up to 250 mL in a graduated flask. Mix thoroughly.

**2.** Titrate 25 mL of the solution with standard hydrochloric acid of approximately 0.1 M concentration using methyl orange, or, better, methyl orange-indigo carmine or bromocresol green as indicator. Two consecutive titrations should agree within 0.05 mL.

**Calculation:-**The weight of anhydrous sodium carbonate, $Na_2CO_3$, which has reacted with the standard hydrochloric acid, can be readily calculated from the equation:

$$Na_2CO_3 + 2HC1 = 2NaC1 + H_2O + CO_2$$

$$106.01 \quad 2 \times 36.46$$

The percentage of $Na_2CO_3$ can then be calculated from the known weight of washing soda employed. A simpler and more general procedure is illustrated by the following example.

Weight of weighing bottle + substance = 16.79 10 g

Weight of weighing bottle + residual substance = 13.0110 g Weight of sample used = 3.7800 g, this was dissolved in water and made up to 250mL.

Titration of 25.00 mL of the carbonate solution with 0.1060M HC1, using methyl orange—indigo carmine as indicator.

l mL 1M HC1 = 0.05300g $Na_2CO_3$

25.93 x 0.1060 = 2.749 mL 1M HC1

2.749 x 0.05300 = 0.1457 g $Na_2CO_3$ in portion titrated.

Weight of washing soda in portion titrated = 3.7800 x 25.0/250 = 0.3780 g

Percentage of $Na_2CO_3$ = 0.1457 x 100/0.3780 = 38.54 per cent

**Discussion:-**

1. What is the washing soda?
2. Why the washing soda contains $Na_2CO_3$?
3. Which the must indicator used in this experiment?

## Experiment No.(11):- Determination of two acids in Soda By Titration

**Theory:-** In this experiment, we will determine the concentration of carbonate and bicarbonate species in sodas using the technique of titration. A primary standard used in this experiment is NaOH for the direct titration of the diprotic acid. A diprotic acid is an acid that yields two $H^+$ ions per acid molecule. Examples of diprotic acids are sulfuric acid, $H_2SO_4$, and carbonic acid, $H_2CO_3$, Color indicators which utilize changes in pH will be used to determine the presence of the different species of the acid.

**Procedure:-**

1. 0.2 g of NaOH pellets were placed in a 50mL volumetric flask and diluted to the mark with distilled water to make an approximate 0.1M solution.
2. 25 mL of each cold, fresh soda was measured in a graduated cylinder.
3. The sample was then placed in a beaker
4. 5 drops of Methyl orange indicator was added to the solution
5. The solution was titrated with NaOH until Color of this indicator changes from yellow to orange to red at pH between 3.1 and 4.4.

**Calculations:-**Calculate the normality of diprotic acid in soda:-

$$(N * V)_{\textbf{diportic acid}} = (N * V)_{\textbf{NaOH}}$$

$$N * 25 = 0.1 * V_{\textbf{burette}}$$

Calculate ppm for $Na_2CO_3$ and $NaHCO_3$

$$ppm\ Na_2CO_3 = N * Eq.WT. * 1000$$

ppm $NaHCO_3$ = N * Eq.WT. *1000

**Discussion:-**

1. What is diprotic acid?
2. Calculate molarity of diprotic acid?
3. What is primary standard used in this experiment?
4. Which organic acids or mineral acids are stronger, why?

## Experiment No.(12):- Double titration

**Theory:-**Double titration is a process was the first titration is used to standardize a titrant and the second titration is used to find the molarity of the unknown solution.

## A:-Analysis of commercial caustic soda:-

Consider a mixture of NaOH(aq) and $Na_2CO_3$(aq). Reaction between HCl(aq) and $Na_2CO_3$(aq) takes place in two stages:-

$$HCl(aq) + Na_2CO_3(aq) \longrightarrow NaHCO_3(aq) + H_2O(l) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$Cl^-(aq) + NaHCO_3(aq) \longrightarrow NaCl(aq) + CO_2(g) + H_2O(l) \quad \ldots\ldots\ldots\ldots .. (2)$$

While that between HCl(aq) and NaOH(aq) completes in only one step:-

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l) \quad \ldots\ldots\ldots\ldots\ldots\ldots .. (3)$$

Reactions (1) and (3) can be indicated by phenolphthalein and that of reaction (2) can be indicated by methyl orange.

Reaction 1 and 3 Evidenced by the first equivalence point between standard solution and both of $OH^-$ and half $CO_3^{-2}$ by using Ph.Ph. indicator, Directory where the color changes from red to colorless. For The remaining half from $CO_3^{-2}$ , added to solution M.O indicator and complete titration with HCl , the color change from yellow to pink and we can see that in reaction (2).

In another method the total alkali (carbonate + hydroxide) is determined by titration with standard acid, using methyl orange as indicator. In a second portion of solution the carbonate is precipitated with a slight excess of barium chloride solution, and, without filtering, the solution is titrated with standard acid using Ph.Ph as indicator. The latter titration gives the hydroxide content, and by subtracting this from the first titration, the Volume of acid required for the carbonate is obtained:-

$$Na_2CO_3 + BaCl_2 \longrightarrow BaCl_2 + 2NaCl$$

**Procedure:-**

1. Transfer 5 ml volume of the mixture solution, with a pipette, to a conical flask then add one or two drops of Ph.PH to this solution and titrate with ( 0.1N HCl) come from the burette gradually with continuous swirling of the solution in the conical flask and near the end point, the acid is added drop by drop. Continue the addition of the acid until the color of the solution passes from red to colorless, record the volume for acid as V1.

2. add one or two drops of methyl orange to this solution and complete the titration with ( 0.1 N HCl) come from the burette until the color change from yellow to pink , record the volume for acid as V2.

3. Repeat the experiment three times and tabulate your results then take the mean of the three readings.

**Calculations:-**A-Calculate the normality and percentages of $OH^-$ in mixture:-

$$(N * V)_{HCl} = (N * V)_{NaOH}$$

$$0.1 * (V1 - V2)_{burette} = N * 1000$$

$$\% \text{ NaOH} = \frac{N * Eq.Wt}{Wt. \text{ of Sample}} * 100$$

B-Calculate the normality and percentages of $CO_3^{-2}$ in mixture:-

$$(N * V)_{HCl} = (N * V)_{Na2\,CO_3}$$

$$(0.1 * 2\,V2)_{burette} = N * 1000$$

$$\% \text{ } Na_2CO_3 = \frac{N * Eq.Wt}{Wt. \text{ of Sample}} * 100$$

**Discussion:-**

1.What is the caustic soda?

2.What is double titration?

3.Why ph.ph indicator used first?

4. Why After addition barium chloride we just use ph.ph indicator ?

## B:-Determination carbonate and bicarbonate in mixture:-

Sodium bicarbonate or sodium hydrogen carbonate is the chemical compound with the formula Na $HCO_3$. Sodium bicarbonate is a white solid that is crystalline but often appears as a fine powder, the salt has many related names such as baking soda, bread soda, cooking soda, and bicarbonate of soda.

This experiment Consider a mixture of carbonate and bicarbonate are titrating with standard solution (0.1 N HCl) by using ph.ph and methyl orange as indicator , after adding ph.ph indicator half of carbonate converted to bicarbonate, but after adding M.O indicator the bicarbonate and half of carbonate converted to $H_2CO_3$ . The $H_2CO_3$ Disintegrate to $CO_2$ and $H_2O$.

$$Na_2CO_3 + HCl \xrightarrow{\text{ph.ph}} NaHCO_3 + NaCl$$
$$NaHCO_3 \qquad\qquad NaHCO_3$$

**pH=9.5 pink** **pH=8.4 colorless**

$$NaHCO_3 + 2HCl \longrightarrow H_2CO_3 + 2NaCl$$
$$NaHCO_3 \qquad\qquad H_2CO_3$$

**pH=8.4 yellow** **pH=4.4 pink**

$$H_2CO_3 \longrightarrow CO_2 + H_2O$$

**Procedure:-**

1. Transfer 5 ml volume of the mixture solution, with a pipette, to a conical flask then add one or two drops of Ph. Ph to this solution and titrate with ( 0.1 N HCl) come from the burette gradually with continuous swirling of the solution in the conical flask and near the end point, the acid is added drop by drop. Continue the addition of the acid until the color of the solution passes from red to colorless, record the volume for acid as V1.

2. add one or two drops of methyl orange to this solution and complete the titration with ( 0.1 N HCl) come from the burette until the color change from yellow to pink , record the volume for acid as V2.

3. Repeat the experiment three times and tabulate your results then take the mean of the three readings

**Calculations:-**

A- Calculate the normality and rate percentages of bicarbonate in mixture:-

$$(N * V)_{HCl} = (N * V)_{NaHCO_3}$$

$$0.1 * (V2 - 2V1)_{burette} = N * 1000$$

$$\% NaHCO_3 = \frac{N * Eq.Wt}{Wt.\ of\ Sample} * 100$$

B- Calculate the normality and rate percentages of $CO_3^{-2}$ in mixture:-

$$(N * V)_{HCl} = (N * V)_{Na_2CO_3}$$

$$(0.1 * 2\ V1)_{burette} = N * 1000$$

$$\% Na_2CO_3 = \frac{N * Eq.Wt}{Wt.\ of\ Sample} * 100$$

**Discussion:-**

1. What is Sodium bicarbonate? What is the basicity difference between $NaHCO_3$ and NaOH?
2. What is the difference between V1 and V2 in experiment A and experiment B?
3. Calculate the conc. Of $Na_2CO_3$ and $NaHCO_3$ by ppm?

## Experiment No.(13):-Determination of bicarbonate in blood by back titration

**Theory:-** About 95% of the total carbon dioxide in human blood exists as $HCO_3^-$, the remainder existing as dissolved $CO_2$. The $HCO_3^-$ concentration, for most clinical work, can be used as a diagnostic aid. It is determined by adding an excess of 0.01 M HC1, to volatilize the $HCO_3^-$ as $CO_2$, swirling to allow the $CO_2$ to escape, and then back-titrating the excess HC1 with 0.01 M NaOH. The 0.01 M HCI and, NaOH solutions are prepared by diluting standardized 0.1 M solutions.

$$HCO_3^- + H^+ \longrightarrow H_2O + CO_2$$

$$\text{excess } H^+ + OH^- \longrightarrow H_2O$$

**Note: The sodium hydroxide solution is a secondary standard, and any errors in standardizing will be represented in the standardizing of the hydrochloric acid, the sodium hydroxide should be used within one week of standardization. If this experiment is done before Experiment 6, this procedure can be used to standardize the sodium hydroxide solu6on for that experiment.**

## Procedure:-Solutions and Chemical's Required:-

1. Provided. 0.1% Phenol red (phenolsulfonaphthalein) solution in 0.003 M NaOH, 1% saline (NaC1) solution in $CO_2$-free water, Anti- foam A (Dow Corning Corp.)

2. To prepare. Standard 0.1 M and 0.01 M HC1 and 0.1 M and 0.01 M NaOH solutions. The molarity of the standard HC1 and standard NaOH needs to be known only to three significant figures. Prepare 250 mL standard 0.1M NaOH. Since only three significant figures are required, you may use one-tenth the amount of KHP for titration, in which case the end point will occur at about 4.0 to 4.5 mL. A 10-mL burette should be used in these titrations. Standardize a 0.1 M HC1 solution by titrating 5.00 mL of it with the standard 0.1M NaOH. The phenol red indicator may be used. If you have only a standard 01 M HC1 solution, use this to standardize 0.1 M NaOH solution.

Prepare 500 mL of 0.01 M HC1 and 0.01 M NaOH solutions by diluting 50 mL of the 0.1 M solutions to 500 mL with the saline solution. These should be prepared fresh on the day of use. The saline aids in the volatilization of the $CO_2$ from the acidified solution by decreasing its solubility.

**Things to do before the Experiment:-Prepare and standardize the 0.1 M HC1 and 0.1 M NaOH. This will require drying primary standard KHP ahead of time if either standard HCI or NaOH is not available.**

- ***The work***:-

1. Preparation of the sample. Either serum or plasma (oxalated or heparinized) may be used for the determination. This may be freshly drawn blood from an animal. (Do not do this yourself; your instructor will supply the sample.) See Chapter 1 for a discussion of the differences between serum, plasma, and whole blood. A 10- to 15-mL sample (20 to 30 mL whole blood) should be adequate for triplicate determinations by a class of 30 students. Fluoride should be added to prevent glycolysis, or breakdown of glucose, which can change the pH. The fluoride inhibits the enzyme catalysis causing glycolysis and stabilizes the pH for about 2 h. The tube used for collecting the sample can be rinsed with a solution of 100 mg sodium heparin plus 4 g sodium fluoride per 100 mL. The sample should be kept anaerobically, that is, stoppered to keep out atmospheric CO. Since the analysis should be done on the day the blood is drawn, the solutions should be prepared ahead of time.

2. Preparation of comparison solution. Prepare a standard for color comparison at the end point as follows. Place 6 mL of 1% saline solution in a 25-ml conical flask and add 0.10 mL serum or plasma. Add two drops phenol red indicator, insert a stopper, and rotate gently to mix the contents. The transition range of this indicator is pH 8.4 to 6.7 (yellow to red). Because of the buffering capacity of the blood, the end point occurs in this range.

3. Titration of the sample. The pooled serum or plasma sample will have been prepared by touching the end of a stirring rod and rotating it in the pooled sample. This will prevent excess foaming when the sample is swirled. Place 0.100 mL of serum or plasma a in a 25-mL Erlenmeyer.

**Note: This determination may be performed on a macro scale using 5.00 mL acid and 1.00 mL sample, or using2.00 mL acid and 0.500 mL sample. In the former case, the back-titration will require about 2.4 mL of 0.01M NaOH, and in the latter case, about 0.7 mL. Flask and add 1.00 mL of 0.01 M HC1 and 4 mL of 1% saline. Swirl the flask vigorously for at least 1 mm to allow the $CO_2$ to escape. Add two drops of indicator and then titrate with 0.01 M NaOH drop wise, but rapidly, until a pink color matching the standard persists for at least 15 S. The NaOH may be added carefully with a graduated 1-mL measuring pipet and read to the nearest 0.01 mL.**

**The normal value of blood bicarbonate is about 26 meq/L (25 to 32 meqlL), or 0.026 meq/mL. Meq $HCO_3$ = mmol $HCO_3$. Since 0.1 mL blood was taken for analysis, it should consume about 0.0026 mmol HC1, or 0.26 mL of 0.01 M HCI. Hence, since 1 mL of 0.01 M HC1 was taken, about 0.74 mL should remain unreacted, and the back-titration should take about 0.7 mL of 0.01 M NaOH.**

**Discussion:-**

1. What is the blood and what does contains?
2. What is the blood pH, why it must be constant?
3. What is the saline solution, why it gives to patent?
4. What is the type of indicator used in this work, why?

## 2// Precipitation titration:-

Volumetric methods based upon the formation of sparingly soluble precipitate are called **precipitation titration**; different titrimetric procedures that take place in solution were discussed. A special type of titrimetric procedures involves the formation of precipitates during the course of a titration. The titrant reacts with the analyte forming an insoluble material and the titration continues till the very last amount of analyte is consumed. The first drop of titrant in excess will react with an indicator resulting in a color change and announcing the termination of the titration. Precipitation titration is a very important; because it is a perfect method for determine halogens and some metal ions. There are three kinds (types) of indicators used in precipitation titration, the first used $K_2CrO_4$

(mohr, formation color precipitation method), the second used fluorescein indicator (fajan method), and the third used $Fe^{+3}$ ion as indicator (volhard method back- titration formation color complex method).

## Experiment No.(14):- Preparation and standardization of 0.1 N $AgNO_3$ solution with sodium chloride (Mohr Method)

**Theory:-**The Mohr method uses chromate ion as an indicator in the titration of chloride ion with silver nitrate. The first excess of titrant results in the formation of a red silver chromate precipitate, which signals the end point.

$$Ag^+ + X^- \longrightarrow AgX + NaNO_3$$

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

$$2AgNO_3 + K_2CrO_4 \longrightarrow AgCrO_4 + 2KNO_3$$

yellow — red ppt.

**Procedure:-**

1-Standardization of silver nitrate solution:-Sodium chloride has a relative molecular mass of 58.44. A 0.05 M solution is prepared by weighing out 0.29 g of the pure dry salt and dissolving it in 50 mL of water in a volumetric flask.

***2.*** Preparation approximately 0.1 N $AgNO_3$: calculate the Wt. in 50 ml of $AgNO_3$ from:-

$$N = \frac{Wt.}{Eq.Wt.} * \frac{1000}{V\ (ml)}$$

$$0.05 = \frac{Wt.}{169} * \frac{1000}{50}$$

Weigh X g of $AgNO_3$ in dry and clean beaker then transfer to 50 ml volumetric flask and complete the volume to the mark with D.W.

***3.*** Transfer 5 ml volume of the(0.02 N NaCl) solution, with a pipette, to a conical flask. Capacity 300 ml.

***4.*** Add 4-5 drops of potassium chromate indicator $K_2CrO_4$ to this solution.

***5.*** Add (0.05 N $AgNO_3$) from the burette gradually with continuous swirling of the solution in the conical flask and near the end point, $AgNO_3$ is added drop by drop. Continue the addition of $AgNO_3$ until appears red Precipitate.

***6.*** Repeat step 2 three time to take the average of volume (V).

***7.*** Find the error of titration process by Transfer 5 ml volume of the D.W, with a pipette, to a conical flask. capacity 300 ml, add 4-5 drops of potassium chromate indicator $K_2CrO_4$ to this solution, Add (0.05 N $AgNO_3$) from the burette gradually with continuous swirling of the solution in the conical flask and near the end point, $AgNO_3$ is added drop by drop. Continue the addition of $AgNO_3$ until upper red Precipitate appears, Recorded the volume (V1).

**Calculations:**-Calculate the normality of $Cl^-$:-

$$(N * V)_{NaCl} = (N * V)_{AgNO3}$$

$$(N * 5) = (0.05 * V - V1)$$

$$conc.(gm/L)_{Cl^-} = N * Eq.Wt$$

**Discussion:-**

**1.** What is the red precipitate?
**2.** What is the name of indicator?
**3.** What is the error of titration process?
**4.** What the second name of this method?
**5.** Why AgCl Precipitate first than $Ag_2CrO_4$?
**6.** Why $AgNO_3$ solution must be standardized first?

## Experiment No.(15):- Determination of Chloride by Volhard's Method (back titration)

**Theory:-** This method uses a back titration with potassium thiocyanate to determine the concentration of chloride ions in a solution. Before the titration an excess volume of a silver nitrate solution is added to the solution containing chloride ions, forming a precipitate of silver chloride. The term ‘excess‘ is used as the moles of silver nitrate added are known to exceed the moles of sodium chloride present in the sample so that all the chloride ions present will react.

$$Ag^+_{(aq)} + Cl^-_{(aq)} \longrightarrow AgCl_{(s)} + Ag^+_{\textbf{excess}}$$

The indicator $Fe^{3+}$ (ferric ion) are then added and the solution is titrated with the potassium thiocyanate solution. The titrate remains pale yellow as the excess (unreacted) silver ions react with the thiocyanate ions to form a silver thiocyanate precipitate.

$$Ag^+_{(aq)\ \textbf{excess}} + SCN^-_{(aq)} \longrightarrow AgSCN_{(s)}$$

Once all the silver ions have reacted, the slightest excess of thiocyanate reacts with $Fe^{3+}$ to form a dark red complex.

$$Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \longrightarrow [FeSCN]^{2+}_{(aq)}$$

**Procedure:-**

1. Weigh 0.2 mg NaCl or KCl, Transfer to a conical flask capacity 250 ml and Dissolve in 50 ml D.W.

2. Added 5-6 drops (6N $HNO_3$).

3. Added 2 ml nitrobenzene.

4. Add excess (V1 ml) 0.05 N $AgNO_3$ by pipette.

5. Add to the conical flask 2 ml from (mohrs salt) Ferric ammonium sulfate solution $NH_4Fe(SO_4)_2.12H_2O$, and titrate with 0.05 N potassium thiocyanate KSCN until upper red/ bloody color appears, Record the volume (V2).

**Calculations:-**Calculate the volume of excess $AgNO_3$:-

$$mEq\ Cl^- = m\ Eq\ AgNO_3 - mEq\ SCN^-$$

$$\frac{Wt.}{Eq.Wt} * 1000 = (N * V) - (N * V)$$

$$\frac{Wt.}{35.40} * 1000 = (0.05 * V1_{\ pipette}) - (0.05 * V2_{\ burette})$$

$$\%Cl^- = \frac{Wt.\ Cl^-}{Wt.\ sample} * 100$$

$$= \frac{Wt.}{0.2\ g} * 100$$

When 0.03546 = eq.wt. for chloride ion.

**Discussion:-**

1. What is back titration?

2. Why nitro benzene is added?

3. What is indicator in this test?

4. Why the nitric acids are added?

5. What is the other name of this method?

# Experiment No.(16):- Determination of Chloride by Fajan's method
## (Adsorption indictors)

**Theory:-**In Fajan method, the end point is detected with a dye that imparts a distinctive color to the silver chloride precipitate. Dichlorofluorescein or Fluorescein (HIn) is commonly used as indicator. As the surface equivalence point is approached and passed, silver ion will become the primary adsorbed the surface of precipitate. The negatively charged dichlorofluorescein or Fluorescein anion ($In^-$) will then on displaces the nitrate ion to become the countering. On being adsorbed, its electronic changes so that it reflects reddish /pink light rather than yellow-green, this signals the end point.

$$AgCl: Ag^+/NO_3^-(s) + HIn\ (yellow) \rightarrow AgCl:Ag^+/In^-\ (pink) + H^+ + NO_3^-$$

**Procedure**:-

1. Transfer 25 ml volume of the NaCl or KCl solution, with a pipette, to a conical flask.

2. Add 5-10 drops Dichlorofluorescein or Fluorescein and 0.1 gm dextrin solution. The color of solution becomes yellow-green.

3. Add 0.0.5 M $AgNO_3$ from the burette gradually with continuous swirling of the solution in the conical flask and near the end point, $AgNO_3$ is added drop by drop. Continue the addition of $AgNO_3$ until appears reddish Precipitate

***Calculations***:-Calculate the molarity of chloride:-

$$(M * V)\mathbf{Cl^-} = (M * V)\ \mathbf{AgNO_3}$$

Calculate PCl:- $PCl = - Log\ [Cl^-]$

-

**Discussion:-**

**1.** What is the HIn?

**2.** Define adsorbed process?

**3.** What is the adsorbed indicator?

**4.** Why dextrin solution is added?

**5.** What is the name of precipitation involved Ag?

**6.** Why the used indicator is called Fluorescein indicator?

# Experiment No.(19):- Determination of potassium

**Theory:-**Potassium may be precipitated with excess of sodium tetraphenylborate solution as potassium tetraphenylborate. The excess of reagent is determined by titration with mercury (II) nitrate solution. The indicator consists of a mixture of iron (III) nitrate and dilute sodium thiocyanate solution. The end-point is revealed by the decolorisation of the iron (III)-thiocyanate complex due to the formation of the colorless mercury (II) thiocyanate. The reaction between mercury(II) nitrate and sodium tetraphenylborate under the experimental conditions used is not quite stoichiometric; hence it is necessary to determine the volume in mL of $Hg(NO_3)_2$ solution equivalent to 1 mL of a $NaB(C_6H_5)_4$ solution. Halides must be absent.

**Procedure**:-

1. Prepare the sodium tetraphenylborate solution by dissolving 6.0 g of the solid in about 200 mL of distilled water in a glass-stoppered bottle.

2. Add about 1 g of moist aluminum hydroxide gel, and shake well at five-minute intervals for about 20 minutes. Filter through a Whatman No. 40 filter paper, pouring the first running's back through the filter if necessary, to ensure a clear filtrate.

3. Add 15 mL of 0.1 M sodium hydroxide to the solution to give a pH of about 9, then make up to 1 L and store the solution in a polyethelene bottle.

4. Prepare a mercury(II) nitrate solution (0.03M) by dissolving 10.3 g recrystallized mercury(II) nitrate, $Hg(N0_3)_2,H_20$, in 800 mL distilled water containing 20 mL 2M nitric acid. Dilute to 1 L in a graduated flask and then standardize by titrating with a standard thiocyanate solution using iron (III) indicator solution.

5. Prepare the indicator solutions for the main titration by dissolving separately 5 g hydrated iron (III) nitrate in 100 mL of distilled water and filtering, and 0.08 g sodium thiocyanate in 100 mL of distilled water.

6. **Standardization**. Pipette 10.0 mL of the sodium tetraphenylborate solution into a 250 mL beaker and add 90 mL water, 2.5 mL 0.1 M nitric acid, 1.0 mL iron (III) nitrate solution, and 10.0 mL sodium thiocyanate solution. Without delay stir the solution mechanically, and then slowly add from a burette 10 drops of mercury (II) nitrate solution. Continue the titration by adding the mercury (II) nitrate solution at a rate of 1—2 drops per second until the color of the indicator is temporarily discharged. Continue the titration more slowly, but maintain the rapid state of stirring. The end point is arbitrarily defined as the point when the indicator color is discharged and fails to reappear for 1 minute. Perform at least three titrations, and calculate the mean

volume of mercury (II) nitrate solution equivalent to 10.0 mL of the sodium tetraphenylborate solution.

7. Pipette 25.0 mL of the potassium ion solution (about 10mg $K^+$) into a 50 mL graduated flask; add 0.5 mL 1 M nitric acid and mix. Introduce 20.0 mL of the sodium tetraphenylborate solution, dilute to the mark, mix, and then pour the mixture into a 150 mL flask provided with a ground stopper. Shake the stoppered flask for 5 minutes on a mechanical shaker to coagulate the precipitate, and then filter most of the solution through a dry Whatman No. 40 filter paper into a dry beaker. Transfer 25.0 mL of the filtrate into a 250 mL conical flask and add 75 mL of water, l.0mL of iron (III) nitrate solution, and 1.0mL of sodium thiocyanate solution. Titrate with the mercury(II) nitrate solution as described above.

****Note. This determination is only suitable for students with analytical experience and should not be attempted by beginners.**

**Calculation:-**

$$\text{mmol } K^+ = \text{mmol } NaB(C_6H_5)_4 - \text{mmol } Hg(NO_3)_2$$

$$(M * V) = (M * V) - (M * V)$$

$$\text{ppm } K^+ = M * A.Wt. * 1000$$

**Discussion:-**

1. Why add NaSCN and $HNO_3$ are added?
2. Write the chemical equation for the titration?
3. What is the chemical formula of tetraphenylborate ?
4. Why NaOH is added and store in a polyethelene bottle?
5. Why aluminum hydroxide gel is added? What it is chemical formula?

## Experiment No.(18):-Determination of silver in silver alloy

**Theory:-** A commercial silver alloy in the form of wire or foil is suitable for this determination.

**Procedure:-**

1. Clean the alloy with emery cloth and weigh it accurately.
2. Place it in a 250 mL conical flask, add 5 mL water and 10 mL concentrated nitric acid; place a funnel in the mouth of the flask to avoid mechanical loss.
3. Warm the flask gently until the alloy has dissolved. Add a little water and boil for 5 minutes in order to expel oxides of nitrogen.
4. Transfer the cold solution quantitatively to a 100 mL graduated flask and make up to the mark with distilled water.
5. Titrate 25 mL portions of the solution with standard 0.1 M thiocyanate.

**Calculation:-**

$$\text{mmol } Ag^{+} = \text{mmol KSCN}$$

$$\frac{\text{Wt.}}{\text{A. Wt.}} * 1000 = M * V$$

$$\frac{\text{Wt.}}{\text{A. Wt.}} * 1000 = 0.1 * V_{\text{burette}}$$

$$\% \text{ Ag in Alloy} = \frac{\text{Wt. Ag}}{\text{Wt. of sample}} * 1000$$

**Discussion:-**

1. Why $HNO_3$ acid is added?
2. Write the chemical equation express the titration reaction?
3. Ag common with two metal in uses, what the other two metals?

## 3//Reduction - Oxidation titration (Re-Dox):-

Is a type of titration based on a redox reaction between the analyte and titrant. Redox titration may involve the use of a redox indicator.A titration characterized by the transfer of electrons from one substance to another (from the reductant to the oxidant) with the end point determined calorimetrically or potentiometrically or by titration.

A redox indicator (also called an oxidation-reduction indicator) is an indicator that undergoes a definite color change at a specific electrode potential.

The requirement for fast and reversible color change means that the oxidation-reduction equilibrium for redox indicator system needs to be established very fast. Therefore only a few classes of organic redox systems can be used for indicator purposes.There are two common types of redox indicators:

- metal-organic complexes (Ex. phenanthroline)
- true organic redox systems (Ex. Methylene blue)

Sometimes colored inorganic oxidants or reductants (Ex. Potassium manganate , Potassium dichromate) are also incorrectly called redox indicators.

Almost all redox indicators with true organic redox systems involve a proton as a participant in their electrochemical reaction.

## Experiment No.(19):-Determination of the Dissolved Oxygen (D.O) in water by iodometric method (winkler method)

**Theory:-**The Winkler Method is a technique used to measure dissolved oxygen in fresh water systems. Dissolved oxygen is used as an indicator of the health of a water body, where higher dissolved oxygen concentrations are correlated with high productivity and little pollution Dissolved oxygen analysis can be used to determine:

- the health or cleanliness of a lake or stream,
- the amount and type of biomass a fresh water system can support,
- the amount of decomposition occurring in the lake or stream.

The **Winkler test** is used to determine the concentration of dissolved oxygen in water samples An excess of manganese(II) salt, and hydroxide ($OH^-$) ions is added to a water sample, then oxygen in water react with $Mn^{2+}$ oxidized by the dissolved oxygen in the water sample into a brown manganese precipitate:-

$$4Mn^{2+} + O_2 + 8OH^- + 2H_2O \longrightarrow 4Mn(OH)_3$$

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The second part of the Winkler test reduces (acidifies) the solution. The precipitate will dissolve back into solution. The acid facilitates the conversion by the brown, Manganese-containing precipitate of the Iodide ion into elemental Iodine.

$$2Mn(OH)_{3(S)} + 3H_2SO_4 \longrightarrow 2Mn^{3+} + 3SO_4^{2-} + 6H_2O$$

$$2Mn^{3+} + 2I^- \longrightarrow 2Mn^{2+} + I_2$$

Iodide Iodine

Thiosulfate is used, with a starch indicator, to titrate the iodine.

$$2NaS_2O_3 + I_2 \xrightarrow{\text{starch}} Na_2S_4O_6 + 2NaI$$

The number of moles of iodine produced= the number of moles of dissolved oxygen in freshwater.

***Procedure:-A-Reagents:-***

1. Manganous sulfate solution: Dissolve 12 g $MnSO_4 \cdot 4H_2O$, 10g $MnSO_4 \cdot 2H_2O$, or 9.1 g $MnSO_4 \cdot H_2O$ in distilled water, filter, and dilute to 25 ml.

2. Alkali-iodide reagent:
Dissolve 12.5 g NaOH (or 17.5 g KOH) and 3.375 g NaI (or 3.75g KI) in distilled water and dilute to 25 ml.

3. Sulfuric acid, $H_2SO_4$, conc.

4. Starch indicator: dissolve 0.2 gm from it in 200 ml D.W.

5. Standard sodium thiosulfate titrant (0.025 N): Dissolve 0.155 g $Na_2S_2O_3 \cdot 5H_2O$ in 25 ml distilled water.

***B-The work:-***

1. To the sample collected in a 250- to 300-mL bottle, add 2 mL $MnSO_4$ solution, followed by 2 mL alkali-iodide reagent. Stopper and mix by inverting bottle a few times. When precipitate has settled sufficiently (to approximately half the bottle volume) to leave clear supernatant above the manganese hydroxide floc, add 2.0 mL conc $H_2SO_4$. Restopper and mix by inverting several times until dissolution is complete.

2. Titrate a volume corresponding to 200 mL original sample after correction for sample loss by displacement with reagents. Thus, for a total of 4 mL (2 mL each) of $MnSO_4$ and alkali-iodide reagents in a 300-mL bottle, titrate 200×300/(300 - 4) = 203 mL.

3. Add a few drops of starch solution and Titrate with 0.025M $Na_2S_2O_3 \cdot 5H_2O$ solution; continue titration to first disappearance of blue color.

**Calculations:-**Calculate the conc. of D.O by ppm***:-***

$$\text{DO as mg / L} = \text{ml of } Na_2S_2O_3.5H_2O \times 2$$

## Discussion:-

1. What is the Winkler Method?
2. What are the redox indicators?
3. What is the Dissolved oxygen?
4. What the advantage is of applied this experiment?

# Experiment No.(20):-Determination of available chloride in hypochlorite

**Theory:-**Most hypochlorite's are normally obtained only in solution, but calcium hypochlorite exists in the solid form in commercial bleaching powder which consists essentially of a mixture of calcium hypochlorite $Ca(OC1)_2$ and the basic chloride $CaC1_2$,$Ca(OH)_2$,$H_2O$; some free slaked lime is usually present. The active constituent is the hypochlorite, which is responsible for the bleaching action. Upon treating bleaching powder with hydrochloric acid, chlorine is liberated: $OCl^- + Cl^- + 2H^+ = C1_2 + H_2O$

The available chlorine refers to the chlorine liberated by the action of dilute acids on the hypochlorite, and is expressed as the percentage by weight in the case of bleaching powder. Commercial bleaching powder contains 36-38 per cent of available chlorine.

Two methods are in common use for the determination of the available chlorine. In the first, the hypochlorite solution or suspension is treated with an excess of a solution of potassium iodide, and strongly acidified with acetic acid:

$$OC1^- + 21^- + 2H^+ = Cl^- + 1_2 + H_2O$$

The liberated iodine is titrated with standard sodium thiosulphate solution. The solution should not be strongly acidified with acetic acid, for the little calcium chlorate which is usually present, by virtue of the decomposition of the hypochlorite, will react slowly with the potassium iodide and liberate iodine:

$$C1O^- + 61^- + 6H^+ = C1^- + 31_2 + 3H_2O$$

In the second method, the hypochlorite solution or suspension is titrated against standard sodium arsenite solution; this is best done by adding an excess of the arsenite solution and then back-titrating with standard iodine solution.

## Procedure:- (iodometric method):-

1. Weigh out accurately about 5.0 g of the bleaching powder into a clean glass mortar. Add a little water, and rub the mixture to a smooth paste. Add a little more water, titration with the pestle, allow the mixture to settle, and pour off the milky liquid into a 500 mL graduated flask.

2. Grind the residue with a little more water, and repeat the operation until the whole of the sample has been transferred to the flask either in solution or in a state of very fine suspension, and the mortar washed quite clean.

3. The flask is then filled to the mark with distilled water, well shaken, and 50.0 mL of the turbid liquid immediately withdrawn with a pipette. This is transferred to a 250 mL conical flask, 25 mL of water added, followed by 2 g of iodate-free potassium iodide (or 20 mL of a 10 per cent solution) and 10 mL of glacial acetic acid.

4. Titrate the liberated iodine with standard 0.1M sodium thiosulphate solution.

**Calculation:-**

$$\text{meq } Cl_2 = \text{meq } Na_2S_2O_3$$

$$\frac{\text{Wt.}}{\text{At. Wt.}} * 1000 = N * V$$

$$\% Cl_2 = \frac{\text{Wt. } Cl_2}{\text{Wt. sample}} * 100$$

**Discussion:-**

1. What is the indicator used, why?
2. Write balance equations for the titration reaction?
3. What is the suspension solution, what is differing from colloidal solution?

## Experiment No.(21):- Preparation and standardization of 0.1 M $Na_2S_2O_3 .5H_2O$

**Theory:-**The oxidation reduction reactions which involve the use of iodine may be divided into two classes as follows:

**a- Iodimetry** (direct method): is the use of $I_2$ as standard oxidizing agent for direct determination of reducing agent (e.g. $S_2O_3^{2-}$, $Sn^{2+}$, ……etc).
**b- Iodometry** (indirect method): is the use of I- for indirect determination of oxidizing agent (e.g. $IO_3^-$, $Cr_2O_7^{2-}$, $MnO_4^-$, $H_2O_2$ …….etc). By addition of known excess of I- where oxidizing agent oxidizes iodide and liberating equivalent amount of iodine which is titrated with standard solution of thiosulphate.
**Iodometry**, also known as **iodometric titration**, is a method of volumetric chemical analysis, a redox titration where the appearance or disappearance of elementary iodine indicates the end point.

**Sodium thiosulfate** $Na_2S_2O_3 \cdot 5H_2O$, although sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$, FW=248.17) can be obtained in high purity, solutions may exhibit some decomposition reactions. Therefore, it is prudent to prepare solutions approximately, and then standardize them with a primary standard reagent.
Directions here are for standardization with $KIO_3$ (Eq. Wt.=214.02/ 6). The $KIO_3$

reacts with excess KI to produce $I_2$, as shown in the equation below:

$$\mathbf{IO_3^- + 5\ I^- + 6\ H_3O^+ \rightarrow 3\ I_2 + 9\ H_2O}$$

And titrate with the $Na_2S_2O_3$ solution with starch indicator until the color change from blue to colorless. $\mathbf{I_2 + 2\ S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2\ I^-}$

The principal reaction is the reduction of iodine to iodide by thiosulfate, it is called **iodometric titration.**

**Procedure:-**

1. Boil 250 ml of distilled $H_2O$ for several minutes, and then cool, for killing bacteria.

2. Weigh 5 gm $Na_2S_2O_3 \cdot 5H_2O$, add to 200 ml the boiled water. 0.5 gm $Na_2CO_3$ and store the solution in the dark a bottle, This solution will not be stable for more than one week.

3. Weigh out approximately 0.15 g $KIO_3$. Quantitatively transfer to a 300-mL volumetric flask and dilute with 50 ml D.W., add 2 g KI and 10 mL of (1M HCl)
4. Fill the burette with $Na_2S_2O_3$ solution and slowly titrate until the solution is pale yellow. At this point, add 3-5 mL of starch solution and continue adding titrant dropwise until the blue dark color just disappears.

5. Repeat step4 three times.

**Calculations:-**

$$\text{m eq } Na_2S_2O_3 = \text{m eq } KIO_3$$

$$(N * V)_{Na2S2O3} = (N * V_{burette})_{KIO3}$$

$$1000 * \frac{\text{Wt. of } Na_2S_2O_3}{\text{Eq.Wt}} = (N * V)_{KIO3}$$

$$\% Na_2S_2O_3 = \frac{\text{Wt.}}{\text{Wt. of sample}} * 100$$

**Discussion**:-

1. Why is sodium carbonate used in the preparation of the sodium thiosulfate solution?

2. What is the **Iodometry**?

3. Why is Boiling water before using it?

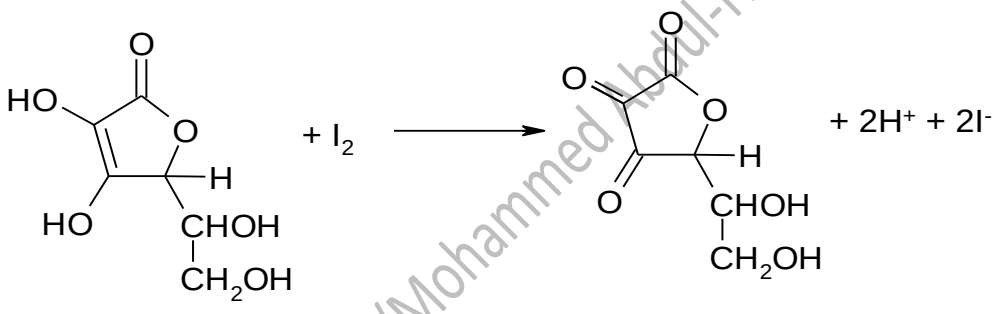
4. Is sodium thiosulfate primary standard solution? Why?

5. What is the difference between **Iodimetry** and **Iodometry**?

6. What is the difference between redox agent and oxidant agent?

## Experiment No.(22):- Determination of vitamin C in the tablet and juice

**Theory:-Vitamin C** (ascorbic acid or its sodium salt) is naturally present in fresh fruit juices or vegetables. It is also used in some pharmaceutical products. The food industry makes use of vitamin C as an anti-oxidation additive in cooked pork meats or canned products to avoid oxygen action.Vitamin C (ascorbic acid) has received much attention lately, as a result of claims that it can cure various diseases, ranging from the common cold to cancer. It is known that vitamin C is an antioxidant and is required for connective tissue synthesis. It is also used for treatment of rheumatoid arthritis. Vitamin C is readily oxidized by iodine in an acidic solution:




L-ascorbic acid L-dehydroxyascorbic acid

Rather than titrating directly with iodine, a known excess of iodine will be generated directly in the solution with the ascorbic acid, according to the following reaction:

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

The excess iodine which did not react with the ascorbic acid will then be back-titrated with standard sodium thiosulfate solution: $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

Iodine forms a complex with starch which is dark blue and the endpoint of the titration can be detected by the disappearance of this color. By knowing the total quantity of iodine formed, and the quantity left after reaction with vitamin C, the amount of iodine reacted with the vitamin C can be calculated.

**Procedure:-A-Determination of vitamin C in the tablet:-**

1. Weigh a vitamin C tablet and grind to a powder with a mortar and pestle.

2. Dissolve the powder in 10-20 mL (0.6M $H_2SO_4$) and carefully transfer to a 500-

mL volumetric flask. Dilute to the mark with distilled water. This is your stock solution.

3. Pipette 10 mL of the stock solution into a conical flask and ***carefully*** add about 0.1 g of oxalic acid.

**WARNING**: Oxalic acid is toxic. Handle it with care, and wash your hands after finishing the experiment.

4. Into this conical flask, pipet 25 mL of the $KIO_3$ solution, and add about 2 g of KI and 10 mL of (0.6M $H_2SO_4$).
5. Perform triplicate titrations with $Na_2S_2O_3$ solution as before, adding 2 mL of starch solution just prior to the endpoint. Record the volume of titrant used.

## B- Determination of vitamin C in the juice:-

1. Use a graduated pipet to measure out 5 ml of juice.

2. Transfer the juice to a clean 125 ml conical flask. Add the following: 50 mL distilled water, 5-10 mL ( 0.6M $H_2SO_4$)
3. Pipette 10 mL of the juice into a conical flask and ***carefully*** add about 0.1 g of oxalic acid.
4. Into this conical flask, pipet 25 mL of the $KIO_3$ solution, and add about 2 g of KI and 10 mL of (0.6-M $H_2SO_4$).
5. Perform triplicate titrations with $Na_2S_2O_3$ solution as before, adding 2 mL of starch solution just prior to the endpoint. Record the volume of titrant used.

**Calculations:-A-Calculate the normality of vitamin C in tablet:-**

$$(N * V)_{\text{vitamin C}} = (N * V)_{Na_2S_2O_3}$$

$$1000 * \frac{\text{Wt. of tablet}}{\text{Eq.Wt of vitamine C}} = 0.03 * V_{\text{burate}}$$

B- **Calculate the molarity of vitamin C in orange juice:-**

$$(N * V)_{\text{vitamin C}} = (N * V)_{Na_2S_2O_3}$$

$$N * 5 = 0.03 * V_{\text{burate}}$$

**Discussion**:-

1. What is back-titration?

2. What is the L-ascorbic acid?

3. Why do you add oxalic acid to the stock solution of the vitamin C?

# Experiment No.(23):-Iiodometric determination of copper in copper sulfate

**Theory:-** Pure copper is used as a primary standard for sodium thiosulfate and is recommended when the thiosulfate is to be used for the determination of copper. Upon addition of excess iodide to a solution of Cu (II), a precipitate of CuI is formed along with $I_2$. The liberated iodine is then titrated with standard sodium thiosulfate.

$$2\ Cu^{2+} + 4\ I^- \rightleftharpoons 2\ CuI(s) + I_2$$

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

**Procedure:-**

1. Weigh 0.6 gm $CuSO_4.\ 5H_2O$.
2. Dissolve in 25 ml D.W.
3. Added 2 ml (5N HCl)
4. Transfer the solution to the conical flask capacity 300 ml and add 75 ml D.W.
5. Add a 5 ml of starch solution and Titrate with 0.025M $Na_2S_2O_3 \cdot 5H_2O$ solution, continue titration to first disappearance of blue color
6. Add 1 gm $NH_4SCN$ or KSCN. Mix well; if the blue color return again, adds another amount from sodium thiosulphate till the white precipitate is appear.
7. Repeat step 7 and 8 three time.

**Calculations:-**Calculate the Rate percentages for Cu in salt:-

$$m\ eq\ CuSO_4 = m\ eq\ Na_2S_2O_3$$

$$(N * V)_{CuSO4} = (N * V)_{Na2S2O3}$$

$$1000 * \frac{\text{Wt. of Cu in salt}}{\text{eq.Wt}} = (N * V)_{Na2S2O3}$$

$$\%\ Cu\ in\ CuSO_4 = \frac{Wt\ Cu\ in\ CuSO_4}{\text{Wt. of Sample}} * 100$$

**Discussion:-** 1. Why we add KI?

2. What is the type of $CuSO_4$ and what is deference between them?
3. Why we add KSCN?
3. Why we add HCl?

# Experiment No.(24):- Determination of Copper in Brass

**Theory:-** Brass (alloy) contains amounts of tin, lead, and zinc (and perhaps minor amount of nickel and iron). The method is relatively simple and applicable to brasses with less than 2% iron.

A weighed sample is treated with nitric acid, which causes the tin to precipitate as a hydrated oxide of uncertain composition evaporation with sulfuric acid to the appearance of sulfur trioxide eliminates the excess nitrate, redissolves the tin compound, and possibly causes the formation of lead sulfate. The pH is adjusted amount of phosphoric acid. An excess of potassium iodide is added, and the liberated iodine is titrated with standard thiosulfate.

**Procedure:-**

1. If so directed, free the metal of foils by treated with an organic solvent, heat in an oven to drive off the solvent.

2. Weight 0.1-0.3 mg sample into 250 ml conical flask, and introduce 5 ml of 6M $HNO_3$ into each.

3. Warm (HOOD) until solution is complete, add 10 ml of conc. $H_2SO_4$, and evaporate (HOOD) until copious white fumes of $SO_3$ are given off.

4. Allow the mixture to cool, cautiously add 30 ml of D.W, boil for 1-2 min, and again cool.

5. Add conc. $NH_3$ dropwise and with thorough mixing to produce the intensely blue $Cu(NH_3)_4^{+2}$, the solution should smell faintly of ammonia (note).

6. Add with dropwise 3M $H_2SO_4$ until the color of the complex just disappear s , and then add 2 ml of 85% $H_3PO_4$. Cool to room temperature.

7. Treat each sample individually from this point on to minimize the air-oxidation of iodide ion. Add 4 g of KI to the sample, and titrate with $Na_2S_2O_3$ until the solution becomes pale yellow.

8. Add 5 ml of starch indicator, and continue the titration until the blue color becomes faint. Add 2 g of KSCN; swirl vigorously for 30 s. complete the titration, using the disappearance of the blue starch/ $I_2$ color as the end point.

**Note: vapors should not be sniffed directly from the flask but instead should be wafted toward the nose with a waving motion of one's hand.**

**Calculation:-**

$$\text{mmol Cu} = \text{mmol } Na_2CO_3$$

$$\frac{\text{Wt.}}{\text{At. Wt.}} * 1000 = (M * V) * \frac{a}{b}$$

$$\text{Cu \%} = \frac{\text{Wt.}}{\text{Wt. sample}} * 1000$$

**Discussion:-**

1. Write balance chemical equation for the titration?
2. Why starch must added after solution become palled- yellow?
3. Why the chemical compound, $HNO_3$, $H_3PO_4$, KI, Starch, KSCN and $NH_3$ are added?

## Experiment No.(25):- Determination of mercury

**Theory:-**The mercury is precipitated as mercury ( I) chloride and the latter is reacted with standard potassium iodate solution:

$$IO_3^- + 2Hg_2Cl_2 + 6H^+ + l3Cl^- = IC1 + 4[HgC1_4]^{-2} + 3H_2O$$

Thus:- $$K1O_3 = 4Hg = 2Hg_2C1_2$$

To determine the purity of a sample of mercury (II) salt, the following procedure in which the compound is reduced with phosphorous (phosphonic) acid may be used; to assay a sample of a mercury (I) salt, the reduction with phosphorous acid is omitted.

**Procedure:-**

**1.** Weigh out accurately about 2.5 g of finely powdered mercury (II) chloride, and dissolve it in 100 mL of water in a graduated flask.

**2.** Shake well. Transfer 25.0 mL of the solution to a conical flask; add 25 mL water, 2 mL 1M hydrochloric acid, and excess of 50 per cent phosphorous (III) acid solution.

**3.** Stir thoroughly and allow standing for 12 hours or more. Filter the precipitated mercury (I) chloride through a quantitative filter paper and wash the precipitate moderately with cold water.

**4.** Transfer the precipitate with the filter paper quantitatively to a 250 mL reagent bottle; add 30 mL concentrated hydrochloric acid, 20 mL water, and 5 mL carbon tetrachloride or chloroform.

**5.** Titrate the mixture with standard 0.025M potassium iodate in the usual manner

$$2HgC1_2 + H_3PO_3 + H_2O = Hg_2C1_2 + 2HC1 + H_3PO_4$$

**Calculation**:-

$$\text{mmol Hg} = \text{mmol } KIO_3 * \frac{\text{mmol Hg}}{\text{mmol } KIO_3}$$

$$\frac{\text{Wt.}}{\text{A. Wt.}} * 1000 = (M * V)\ KIO_3 * \frac{4}{1}$$

**Discussion:-**

1. Why phosphoric acid is added?
2. What is the type of indicator used?
3. What is the oxidation state of mercury?
4. Why HCl and carbon tetrachloride are added?

## Experiment No.(26):- Determination Antimony in stibnite (Iodimetric titration)

**Theory:-**The analysis of stibnite, a common antimony ore, is atypical application of iodimetry and is based upon the oxidation of $Sb^{+3}$ to $Sb^{+5}$ :-

$$SbO_3^{-3} + I_2 + H_2O \rightleftharpoons SbO_4^{-3} + 2I^- + 2H^+$$

The position of this equilibrium is strongly dependent upon the hydrogen ion concentration. In order to force the reaction to the right, it is common practice to carry out the titration in the presence of an excess of sodium hydrogen carbonate, which consumes the hydrogen ions as they form.

**Procedure:-**

1. Dry the unknown at 110 $^{o}$C for 1h, and allow it to cool in a desiccator.
2. Weigh individual samples (note1) into 500 ml conical flask.
3. Introduce 0.3 g of KCl and 10 ml of concentrated HCl to each flask.
4. Heat the mixture (HOOD) just below boiling until only white or slightly gray residues of $SiO_2$ remain.

5. Add 3 g of tartaric acid to each sample and heat for an additional 10 to 15 min.

6. With swirling, add water (note2) from a pipet or burette until the volume is about 100 ml.

7. If reddish $Sb_2S_3$ form, discontinue dilution and heat further to eliminate $H_2S$,add more HCl if necessary.

8. Add 3 drops of ph.ph indicator, and neutralize with 6 M NaOH to the first faint pink of the indicator.

9. Discharge the color by the dropwise addition of 6 M HCl, and then add 1 ml in excess.

10. Introduce 4 -5 g of $NaHCO_3$ , taking care to avoid losses of solution by spattering during the addition.

11. Add 5 ml of starch indicator, rine down the inside of the flask, and titrate with standard 0.05 M $I_2$ to the first blue color that persists for 30 S.

**Note1: samples should contain between 1.5 and 2 mmol of antimony, consult with the instructor for an appropriate sample size. Weight to the nearest milligram is adequate for samples larger than 1 g.**

**Note2: the slow addition of water, with efficient stirring, is essential to prevent the formation of SbOCl.**

**Calculation:-**

$$\text{mmol Sb} = \text{mmol } I_2 * \frac{a}{b}$$

$$\frac{\text{Wt.}}{\text{At. Wt.}} * 1000 = (M * V) * \frac{a}{b}$$

$$\% \text{ Sb} = \frac{\text{Wt. Sb}}{\text{Wt. sample}} * 100$$

**Discussion:-**

1. How many type of redox – oxidation indicator are?

2. Calculate the equivalent weight for $Na_2CO_3$ as salt and as reducing agent?

## Experiment No.(27):-Determination of iron in its ore

**Theory:-**Potassium dichromate can be obtained pure, it is stable up to its fusion point, and it is therefore an excellent primary standard. Standard solutions of exactly known concentration can be prepared by weighing out the pure dry salt and dissolving it in the proper volume of water. Furthermore, the aqueous solutions are stable indefinitely if

adequately protected from evaporation. Potassium dichromate is used only in acid solution, and is reduced rapidly at the ordinary temperature to a green chromium (III) salt. It is not reduced by cold hydrochloric acid. Potassium dichromate is therefore of particular value in the determination of iron in iron ores: the ore is usually dissolved in hydrochloric acid, the iron (III) reduced to iron (II), and the solution then titrated with standard dichromate solution: $Cr_2O_7^{-2} + 6Fe^{+2} + 14H^+ = 2Cr^{+3} + 6Fe^{+3} + 7H_2O$

In acid solution, the reduction of potassium dichromate may be represented as:

$$Cr_2O_7^{-2} + 14H^+ + 6e = 2Cr^{+3} + 7H_2O$$

**Procedure:-**

1. With metallic iron. Use iron wire of 99.9 per cent assay value (Note 1). Insert a well-fitting rubber stopper provided with a bent delivery tube into a 500 mL conical flask and clamp the flask in a retort stand in an inclined position, the tube being so bent as to dip into a small beaker containing saturated sodium hydrogen carbonate solution or 20 per cent potassium hydrogen carbonate solution (prepared from the solids) .

2. Place 100 mL 1.5 M sulphuric acid (from 92 mL water and 8 mL concentrated sulphuric acid) in the flask,

3. And add 0.5-1 g sodium hydrogen carbonate in two portions; the carbon dioxide produced will drive out the air. Meanwhile, weigh out accurately about 0.2 g of iron wire, place it quickly into the flask, replace the stopper and bent tube, and warm gently until the iron has dissolved completely. Cool the flask rapidly under a stream of cold water, with the delivery tube still dipping into the solution in the beaker (Note 2).

4. Titrate the cooled solution immediately with the dichromate solution, using either sodium diphenylamine sulphonate or N-phenylanthranilic acid as indicator. If the former is selected, add 6-8 drops of the indicator, followed by 5 mL of syrupy phosphoric (V) acid: titrate slowly with the dichromate solution, stirring well, until the pure green colour changes to a grey-green. Then add the dichromate solution drop wise until the first tinge of blue-violet, which remains permanent on shaking, appears. If the latter indicator is selected, add 200 mL of 1M sulphuric acid, then 0.5 mL of the indicator; add the dichromate solution, with shaking until the color changes from green to violet-red (Note 3): 1 mole $K_2Cr_2O_7$ = 6 moles Fe

****Notes. (1) Iron wire of 99.9 per cent purity is available commercially and is a suitable analytical standard. If the wire exhibits any sign of rust, it should be drawn between two pieces of fine emery cloth, and then wiped with a clean; dry cloth before use.**

**(2) As the flask cools, the hydrogen carbonate solution is automatically drawn in until the pressure of the carbon dioxide inside the flask is equal to the atmospheric pressure.**

**(3) The standardization may also be effected with ethylenediammonium iron (II) sulphate.**

**Calculation:-**

$$\text{mmol } K_2Cr_2O_7 = \text{mmol Fe} * \frac{\text{mole } K_2Cr_2O_7}{\text{mole Fe}}$$

$$M * V = \frac{\text{Wt.}}{\text{A. Wt.}} \quad \frac{* 1}{6}$$

$$\% \text{ Fe in ore} = \frac{\text{Wt. Fe}}{\text{Wt. of sample}} * 100$$

**Discussion:-**

1. Why $H_2SO_4$ is added?
2. Why $NaHCO_3$ or $KHCO_3$ is added?
3. In which medium $K_2Cr_2O_7$ is used and why?
4. Why $K_2Cr_2O_7$ is considered primary standard material?

## Experiment No.(28):-Determination of Chemical Oxygen Demand

**Theory**:- One very important application of potassium dichromate is in a back-titration for the environmental determination of the amount of oxygen required to oxidize all the organic material in a sample of impure water, such as sewage effluent. This is known as the chemical oxygen demand (C.O.D.) and is expressed in terms of milligrams of oxygen required per litter of water, mg $L^{-1}$ . The analysis of the impure water sample is carried out in parallel with a blank determination on pure, double-distilled water.

**Procedure:-**

1. Place a 50 mL volume of the water sample in a 250 mL conical flask with a ground-glass neck which can be fitted with a water condenser for refluxing.
2. Add 1 g of mercury (II) sulphate, followed by 80mL of a silver sulphate/sulphuric acid solution (Note 1).
3. Then add 10 mL of approximately 0.00833M standard potassium dichromate solution (Note 2).
4. Fit the flask with the reflux condenser and boil the mixture for 15 minutes. On cooling rinse the inside of the condenser with 50 mL of water into the flask contents.

5. Add either diphenylamine indicator (1 mL) or ferroin indicator and titrate with 0.025M ammonium iron (II) sulphate solution (Note 3). Diphenylamine gives a color changes from blue to green at the end-point, whilst that for ferroin is blue-green to red-brown. Call this titration A mL.

6. Repeat the back-titration for the blank(Titration B mL). The difference between the two values is the amount of potassium dichromate used up in the oxidation.

**Calculation:**-The C.O.D. is calculated from the relationship:

$$\textbf{C.O.D. = (A-B) X 0.2 X 20 mgL}^{-1}$$

As a 1 mL difference between the titrations corresponds to 0.2mg of oxygen required by the 50 mL sample (a correction must, of course, be made if solutions of slightly different molarities are employed); see Note 4.

****Notes. (1) This solution is prepared by dissolving 5 g of silver sulphate in 500 mL of concentrated sulphuric acid.**

**(2) The required concentration is obtained by weighing out 1.225 g of potassium dichromate and diluting to 500 mL with de-ionized water in a graduated flask.**

**(3) Dissolve 4.9 g of ammonium iron (II) sulphate heptahydrate in 150 mL of water and add 2.5 mL of concentrated sulphuric acid. Dilute the solution to 500 mL in a graduated flask.**

**(4) This method gives high results with samples possessing high chloride content due to reaction between the mercury (II) sulphate and the chloride ions. In these cases the problem can be overcome by following a procedure using chromium(III) potassium sulphate, Cr(III) $K(SO_4)_2.12H_2O$.**

**Discussion:-**

1. What is the C.O.D?
2. What is the back titration?
3. Why $HgSO_4$ and $Ag_2SO_4$ are added?
4. What is the Potassium dichromate color and what difference to $K_2CrO_4$?

## Experiment No.(29):- Standardization of cerium(IV) sulphate solutions

### Method A:-Standardization with arsenic (III) oxide:-

**Theory**:-Cerium (IV) sulphate is a powerful oxidizing agent; the most trustworthy method for standardizing cerium (IV) sulphate solutions is with pure arsenic (III) oxide. The reaction between cerium (IV) sulphate solution and arsenic (III) oxide is very slow at the ambient temperature; it is necessary to add a trace of osmium tetroxide as catalyst. The arsenic(III) oxide is dissolved in sodium hydroxide solution, the solution acidified with dilute sulphuric acid, and after adding 2 drops of an ‘osmic acid’ solution prepared

by dissolving 0.1 g osmium tetroxide in 40 mL of 0.05M sulphuric acid, and the indicator (1-2 drops ferroin or 0.5 mL N-phenylanthranilic acid), it is titrated with the cerium(IV) sulphate solution to the first sharp color change: orange-red to very pale blue or yellowish-green to purple respectively.

$$2Ce^{+4} + H_3AsO_3 + H_2O = 2Ce^{+3} + H_3AsO_4 + 2H^+$$

**Procedure:-**

1. Weigh out accurately about 0.1 g of arsenic (III) oxide, previously dried at 105-110°C for 1-2 hours, and transfer to a 300mL beaker or to a 300 mL conical flask.

2. Add 10 mL of approx. 2M sodium hydroxide solution, and warm the mixture gently until the arsenic (III) oxide has completely dissolved.

3. Cool to room temperature, and add 50 mL water, followed by 12.5 mL 2.5M sulphuric acid.

4. Then add 3 drops 0.01 M osmium tetroxide solution (0.25 g osmium tetroxide (care! fume cupboard) dissolved in 100 mL 0.05M sulphuric acid) and 0.5 mL N-phenylanthranilic acid indicator (or 1-2 drops of ferroin).

5. Titrate with the 0.1 M cerium (IV) sulphate solution until the first sharp color change occurs.

6. Repeat with two other samples of approximately equal weight of arsenic ( III) oxide.

**Calculation:**-Calculate the molarity of $Ce^{+4}$:-

$$\text{mmol } Ce^{+4} = \text{mmol } H_3AsO_3 * 2$$

$$M * V = \left(\frac{Wt.}{M.Wt.} * 1000\right) * 2$$

**Method-B:-Standardization with sodium oxalate**:-

**Theory**:-Standardization may also be carried out with sodium oxalate; in this case, an indirect procedure must be used as the redox indicators are themselves oxidized at the elevated temperatures which are necessary. The procedure, therefore, is to add an excess of the cerium (IV) solution, and then, after cooling, the excess is determined by back-titration with an iron(II) solution. It is possible to carry out a direct titration of the sodium oxalate if a potentiometric procedure is used.

**Procedure:-A:-Potentiometric method:-**

Prepare an approximately 0.1 M solution of ammonium iron(II) sulphate in dilute sulphuric acid and titrate with the cerium(IV) sulphate solution using ferroin indicator.

**B-Titrimetric method:-**

1. Weigh out accurately about 0.2 g sodium oxalate into a 250 mL conical flask and add 25-30mL 1M sulphuric acid.

2. Heat the solution to about 60°C and then add about 30 mL of the cerium(IV) solution to be standardized drop wise, adding the solution as rapidly as possible consistent with drop formation.

3. Re-heat the solution to 60 °C, and then add a further 10 mL of the cerium(IV) solution. Allow to stand for three minutes, then cool and back-titrate the excess cerium (IV) with the iron (II) solution using ferroin as indicator.

4. Practically all the determinations described under potassium permanganate and potassium dichromate may be carried out with cerium (IV) sulphate. Use is made of the various indicators already detailed and also, in some cases where great accuracy is not required, of the pale yellow color produced by the cerium (IV) sulphate itself. Only a few determinations will, therefore, be considered in some detail.

**Calculation**:-

$$\textbf{\textit{A}}: \text{m Eq } Ce^{+4} = \text{m Eq } Fe^{+2}$$

$$N * V = N * V$$

$$\textbf{\textit{B:}}\ \text{m Eq } Na_2C_2O_4 = \text{m Eq } Ce^{+4} - \text{m Eq } Fe^{+2}$$

$$\frac{\text{Wt.}}{\text{Eq. Wt}} * 1000 = (N * V) - (N * V)$$

**Discussion:-**

1. Why $H_2SO_4$ is added?

2. Why must heat the solution rather than cooled?

3. The solution of $Ce^{+4}$ must be standardized why?

4. What is the chemical name and molecular formula of ferion indicator?

## Experiment No.(30):-Determination of nitrites

**Theory**:- Satisfactory results are obtained by adding the nitrite solution to excess of standard 0.1 M cerium (IV) sulphate, and determining the excess of cerium (IV) sulphate with a standard iron(II) solution: $2Ce^{+4} + NO_2^- + H_2O = 2Ce^{+3} + NO_3^- + 2H^+$

For practice, determine the percentage of NO in potassium nitrite, or the purity of sodium nitrite, preferably of analytical-grade quality.

**Procedure**:-

1. Weigh out accurately about 1.5 g of sodium nitrite and dissolve it in 500 mL of boiled-out water in a graduated flask.

2. Shake thoroughly. Place 50 mL of standard 0.1M cerium (IV) sulphate in a conical flask, and add l0 mL of 2M sulphuric acid.

3. Transfer 25 mL of the nitrite solution to this flask by means of a pipette, and keep the tip of the pipette below the surface of the liquid during the addition.

4. Allow to stand for 5 minutes, and titrate the excess of cerium (IV) sulphate with standard 0.1M ammonium iron (II) sulphate, using ferroin or N-phenylanthranilic acid as indicator.

5. Repeat the titration with two further portions of the nitrite solution.

6. Standardize the iron solution by titrating 25 mL of it with the cerium(IV) solution in the presence of dilute sulphuric acid.

7. Determine the volume of the standard cerium (IV) sulphate solution which has reacted with the nitrite solution, and there from calculate the purity of the sodium nitrite employed.

****Note. Cerium (IV) sulphate may also be used for the following analyses.**

**Hydrogen peroxide . The diluted solution, which may contain nitric or hydrochloric acid in any concentration between 0.5 and 3M or sulphuric acid in the concentration range 0.25 to 1.5M, is titrated directly with standard cerium (IV) sulphate solution, using ferroin or N-phenylanthranilic acid as indicator. The reaction is:** $2Ce^{+4} + H_2O_2 = 2Ce^{+3} + O_2 + 2H^+$

**Persuiphate (peroxydisuiphate,). Persulphate cannot be determined directly by reduction with iron (II) because the reaction is too slow:** $S_2O_8^{-2} + 2Fe^{2+} = 2SO_4^{-2} + 2Fe^{+3}$

**An excess of a standard solution of iron (II) must therefore be added and the excess back-titrated with standard cerium (IV) sulphate solution. Erratic results are obtained, depending upon the exact experimental conditions, because of induced reactions leading to oxidation by air of iron (II) ion or to decomposition of the persulphate; these induced reactions are inhibited by bromide ion in concentrations not exceeding 1 M and, under these conditions, the determination may be carried out in the presence of organic matter.**

**To 25.0 mL of 0.01-0.015M persulphate solution in a 150 mL conical flask, add 7 mE of 5M sodium bromide solution and 2 mL of 3M sulphuric acid. Stopper the flask. Swirl the contents, then add excess of 0.05M ammonium iron (II) sulphate (15.0 mL), and allow standing for 20 minutes. Add 1 ml of 0.001 M ferroin indicator, and titrate the excess of $Fe^{+2}$ ion with 0.02M cerium(IV) sulphate in 0.5 M sulphuric acid to the first colour change from orange to yellow.**

**Hexacyanoferrate(II). This can be determined by titration in 1M $H_2SO_4$ using N-phenylanthranilic acid.**

**Calculation:-**

$$m\ Eq\ NaNO_3 = m\ Eq\ Ce^{+4} - m\ Eq\ Fe^{+2}$$

$$\frac{Wt.}{Eq.\ Wt.} * 1000 = (N * V) - (N * V)$$

$$purityvNaNO_3 = \frac{Wt.\ of\ NaNO_3}{Wt.\ of\ sample} * 100$$

**Discussion:-**

1. Why boiled the solution?
2. What is the kind of ferion indicator?
3. The titration must be taken in $H_2SO_4$ medium, why?

## Experiment No.(31):- Determination of iron ($Fe^{+2}$)

**Theory:-**Permanganate ion is strong oxidation reagent, half – reaction for the permanganate is:

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O \quad E^o = 1.51V$$

Permanganate solution decomposes slowly and thus require occasional restandardization.

Aqueous solution of permanganate is not stable because the ion tends to oxidize water:

$$4MnO_4^- + 2H_2O \longrightarrow 4MnO_2 + 3O_2 + 4OH^-$$

The reaction between iron and permanganate performed in acidic medium:

$$MnO_4^- + 5Fe^{2+} + 8\ H^+ \longrightarrow Mn^{2+} + 5\ Fe^{3+} + 4H_2O$$

**Procedure:-**

**A-Prepare 0.1 N oxalic acid in 50 ml volumetric flask**.

$$0.1 = \frac{Wt.}{Eq.Wt.} * \frac{1000}{50}$$

**B-Prepare ( 50 ml) 0.1 N $KMNO_4$:-**

$$0.1 = \frac{Wt.}{Eq.Wt.} * \frac{1000}{50}$$

Weigh 0.6 g $KMnO_4$. Dissolve with D.W in volumetric flask capacity 50 ml. Heat the solution for one hour, filtrate the solution with glass wool.

**C- Standarazation of $KMNO_4$ solution:-**

1. Transfer 5 ml from oxalic acid , with pipette, to conical flask capacity 300 ml
2. Add 5 ml dilute sulphuric acid.
3. Heat the mixture on the water bath for 5 min.
4. Titration against $KMNO_4$ until the faint pink color is appear.
5. Repeat step 3 three time.
6. Calculate the normality of permanganate

$$(N * V)\ KMNO_4 = (N * V)H_2C_2O_4$$

$$N * V = 0.1 * 5$$

**D-Determination of $FeSO_4$ solution:-**

1. Transfer 10 ml from $FeSO_4$.
2. add 5 ml dilute sulphuric acid,
3. Titration against $KMNO_4$ until the faint pink color is appear
4. Repeat this step three times.
5. Calculate the normality of $FeSO_4$:-

$$(N * V)\ KMNO_4 = (N * V)FeSO_4$$

$$N * V = ? * 10$$

**Discussion**:-

1. Why is potassium permanganate not used as a primary standard?

2. Not use indicator why?

3. Added sulphuric acid why?

4. Heat and filtrate the mixture why?

5. Why is the color of solution change from colorless to pink?

6. What equivalent weight of $KMNO_4$ in acidic, basic and neutral medium?

## Experiment No.(32):- Determination phenol by Bromination

**Theory:-**The phenol content of wastewaters from manufacturing processes is conveniently determined by mixing the sample with a measured excess of standard bromated followed by an excess of bromide. The bromine liberated upon acidification reacts with the phenol:-

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

$$C_6H_5OH + 3Br_2 \longrightarrow C_6H_2Br_3OH + 3H^+ + 3Br^-$$

After the bromination is complete, the excess bromine is determined employing the procedure used for the standardization.

**Procedure:-**

1. Transfer a sample containing between 1-1.5 mmol of phenol to 250 ml volumetric flask, dilute to the mark with water.

2. Pipette 25 ml aliquots of the diluted sample into 250 ml conical flask, and add 25 ml aliquots of standard $KBrO_3$ solution.

3. Add about 1 g of KBr and about 5 ml of 3 M $H_2SO_4$ to each flask. Stopper each flask immediately after acidification to prevent the loss of $Br_2$.mix and let stand for about 10 min. swirl the solution until the KBr has dissolved.

4. Titrate with standard 0.05 M $Na_2S_2O_3$ until the solution is pale yellow. Add 5 ml of starch indicator, and complete the titration.

**Calculation:-**

$$\text{mmol phenol} = \text{mmol } Na_2S_2O_3 * \frac{a}{b}$$

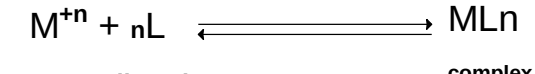
$$\text{mmol phenol} = (M * V)\frac{a}{b}$$

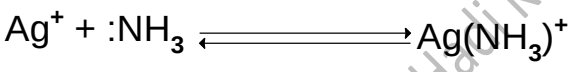
**Discussion:-**

1. Form which organic compound phenol to be considered?
2. Calculate the normality of 10% KBr solution?
3. Why $H_2SO_4$, KBr, KI and $KBrO_3$ are added?

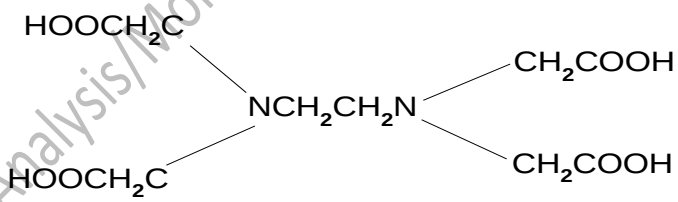
## 4// Complex –formation Titration:-

Most metal ions react with electron- pair donors to form coordination compounds or complex ion.The donor species or **ligand** must have at least one pair of unshared electrons available for bond formation. Water, ammonia, and halide ions are common inorganic ligands.




The **coordination number** of a cation is the number of covalent bonds that a cation tends to form with electron donor groups.Titrimetric methods based upon complex formation.A ligand that has more than two donor group chelating agents are known. Like EDTA (Ethylene di amine tetra acetic acid)




The use of a metal ion indicator in an EDTA titration may be written as:

$$M\text{-}In + EDTA = M\text{-}EDTA + In$$

This reaction will proceed if the metal-indicator complex M-In is less stable than the metal-EDTA complex M-EDTA. The former dissociates to a limited extent, and during the titration the free metal ions are progressively complexed by the EDTA until ultimately the metal is displaced from the complex M-In to leave the free indicator (In).

The majority for EDTA titration is Eriochrome black T, This substance is sodium 1-(1- hydroxy-2-naphthylazo) -6-nitro-2-naphthol-4-sulphonate. In strongly acidic solutions the dye tends to polymerise to a red-brown product, and consequently the indicator is rarely applied in titrations of solutions more acidic than pH = 6.5.

# Experiment No.(33):- Determination of water hardness

**Theory:-**Water hardness was defined in terms of the capacity of cation in the water to replace the sodium or potassium in soaps and form sparingly soluble products.

Water hardness determined by an EDTA titration after the sample has been buffered to pH 10. Mg, which forms the least stable EDTA complex of all of cation in water sample, is not titrated untile enough reagent has been added to complex all of other cation in the sample. Therefore, Mg ion indicator such as EBT, can serve as indicator in water hardness titration. ( Indicator EBT = $H_3In$ , EDTA= $H_4Y$).

$$Ca^{2+} + H2Y^{-2} \longrightarrow CaY^{2-} + 2H^{+}$$

$$Ca^{2+} + MgY^{2-} \longrightarrow CaY^{2-} + Mg^{2+}$$

$$Mg^{2+} + HIn^{2-} \longrightarrow MgIn^{-} + H^{+}$$

$$MgIn^{-} + H_2Y^{2-} \longrightarrow MgY^{2-} + HIn^{2+} + H^{+}$$

**Red colorless colorless blue**

**Procedure:-**

1. Dry 3 gm $Na_2EDTA.2H_2O$ ($Na_2H_2Y.2H_2O$) at 80 $C^0$ for 2 hour, cold in dissector for 30 min.

2. Take 0. 2 gm and transfer into 50 ml volumetric flask after dissolved in 40 ml D.W(de-ionized), stirring, and complete the volume to the market.

3. Calculate the molarity of EDTA:-

$$M_{EDTA} = \frac{\text{Wt. of } Na_2H_2Y.2H_2O \text{ (gm)}}{\text{M.wt } Na_2H_2Y.2H_2O \text{( g/mol)}} * \frac{1000}{50}$$

4. Titration: to 50 ml sample of water add 2 ml buffering solution ($NH_4Cl + NH_4OH$ , pH=10) and 30-40 mg EBT indicator , titrate with standard 0.01 M EDTA until the color changes from red to blue, should there be no Mg present in the sample of water it is necessary to add 0.1 ml Mg-EDTA solution (0.1 M) before adding indicator. The total hardness is expressed in parts of $CaCO_3$ per million of water. (note: if the water contains traces of interfering ions, then 4 ml of buffering solution should be added, followed by 30 mg hydroxyl ammonium chloride and then 50 mg A.R potassium cyanide before adding the indicator.

**Calculation:-**Calculate total hardness is expressed in parts of $CaCO_3$ per million of water:-

$$ppm(mg/l) = \frac{Wt.(gm)}{V(ml)} * 10^6 \Longrightarrow \frac{Wt.(gm)}{V(ml)} = \frac{ppm\ (mg/l)}{10^6} \quad ...1$$

$$(M * V)CaCO_3 = (M * V)EDTA$$

$$\frac{Wt.(gm)}{M.Wt_{(CaCO3)}} * \frac{1000}{V\ (ml)} * V_{(sample)} = (M * V)\ EDTA \quad ...2$$

Put eq. (1) in eq.( 2), we have:-

$$\frac{ppm(mg/l)}{10^3} * \frac{1}{M.Wt} * V_{(sample)} = (M * V)\ EDTA$$

$$ppm(mg/l) = \frac{(M * V)EDTA * 10^3 * 109.09}{50\ ml}$$

**Discussion:-**

1. Why Mg-EDTA is added?
2. What is the de-ionized water?
3. What is the coordination number?
4. What is the EBT, EDTA, and ligand?
5. How many type of hardness and must be made?

## Experiment No.(34):- Determination of Iron (III): direct titration

**Theory:-**The end point in an EDTA titration may sometimes be detected by changes in redox potential, and hence by the use of appropriate redox indicators. An excellent example is variamine blue (4- methoxy-4'-aminodiphenylamine), which may be employed in the complexometric titration of iron (III). When a mixture of iron (II) and (III) is titrated with EDTA the latter disappears first. As soon as an amount of the **complexing** agent equivalent to the concentration of iron(III) has been added, Fe(III) increases abruptly and consequently there is a sudden decrease in the redox potential; the end point can therefore be detected either potentiometrically or with a redox indicator.

**Procedure:-**

1. Prepare the indicator solution by dissolving 1 g variamine blue in 100 mL de-ionized water: as already pointed out, variamine blue acts as a redox indicator.

2. Pipette 25 mL iron (III) solution (0.05M) into a conical flask and dilute to 100mL with de-ionized water.

3. Adjust the pH to 2-3; Congo red paper may be used to the first perceptible color change.

4. Add 5 drops of the indicator solution, warm the contents of the flask to 40 °C, and titrate with standard (0.05M) EDTA solution until the initial blue colour of the solution turns grey just before the end point, and with the final drop of reagent changes to yellow. This particular titration is well adapted to be carried out potentiometrically.

**Calculation**:-

$$\text{mmol } Fe^{+3} = \text{mmol EDTA}$$

$$(M * V)_{Fe+3} = (M * V)_{EDTA}$$

$$P\ Fe^{+3} = - \text{Log } [Fe^{+3}]$$

**Discussion:-**

1. What is the type indicator used?

2. How many donated electron in EDTA molecule?

3. Write chemical equations to express reaction the titration?

4. What is the chemical name of EDTA and it is acidic formula?

## Experiment No.(35):-Determination of nickel in presence of iron : analysis of nickel steel

**Theory:**-Nickel may be determined in the presence of a large excess of iron (III) in weakly acidic solution by adding EDTA and triethanolamine; the intense brown precipitate dissolves upon the addition of aqueous sodium hydroxide to yield a colorless solution. The iron (III) is present as the triethanolamine complex and only the nickel is complexed by the EDTA. The excess of EDTA is back-titrated with standard calcium chloride solution in the presence of thymolphthalexone indicator. The color change is from colorless or very pale blue to an intense blue. The nickel-EDTA complex has a faint blue color; the solution should contain less than 35 mg of nickel per 100 mL.

In the back-titration small amounts of copper and zinc and trace amounts of manganese are quantitatively displaced from the EDTA and are complexed by the triethanolamine:

small quantities of cobalt are converted into a triethanolamine complex during the titration. Relatively high concentrations of copper can be masked in the alkaline medium by the addition of thioglycollic acid until colorless. Manganese, if present in quantities of more than 1 mg, may be oxidized by air and forms a manganese (III)-triethanolamine complex, which is intensely green in color; this does not occur if a little hydroxylammonium chloride solution is added.

**Procedure:-**

1. Prepare a standard calcium chloride solution (0.01M) by dissolving 1.000 g of calcium carbonate in the minimum volume of dilute hydrochloric acid and diluting to 1 L with de-ionized water in a graduated flask. Also prepare a 20 per cent aqueous solution of triethanolamine.

2. Weigh out accurately a 1.0 g sample of the nickel steel and dissolve it in the minimum volume of concentrated hydrochloric acid (about 15 mL) to which a little concentrated nitric acid (Ca 1 mL) has been added.

3. Dilute to 250 mL in a graduated flask. Pipette 25.0 mL of this solution into a conical flask; add 25.0mL of 0.01M EDTA and l0mL of triethanolamine solution.

4. Introduce1 M sodium hydroxide solution, with stirring, until the pH of the solution is 11.6 (use a pH meter).

5. Dilute to about 250 mL. Add about 0.05 g of the thymolphthalexone/potassium nitrate mixture; the solution acquires a very pale blue color.

6. Titrate with 0.01M calcium chloride solution until the color changes to an intense blue. If it is felt that the end point color change is not sufficiently distinct, add a further small amount of the indicator, a known volume of 0.01 M EDTA and titrate again with 0.01 M calcium chloride.

**Calculation:-**

$$\text{mmol Ni} = \text{mmol EDTA}$$

$$\left(\frac{\text{Wt.}}{\text{A.Wt.}} * 1000\right)_{\text{Ni}} = (\text{M} * \text{V})_{\text{EDTA}}$$

$$\%\text{Ni in Alloy} = \frac{\text{Wt. Ni}}{\text{Wt. sample}} * 100$$

**Discussion:-**

1. Why the EDTA does react with Ni but not with $Fe^{+3}$?

2. What do you mean be the selective reaction (titration or determination)?

3. What is the type of indicator used in this titration?

4. Why $CaCl_2$ ,HCl , and tri ethanol amine are added?

5. Write balance equation to express the titration reaction?

## Experiment No.(36):-Determination of lead and tin in mixture :analysis of solder

**Theory:-**A mixture of tin(IV) and lead(II) ions may be complexed by adding an excess of standard EDTA solution, the excess EDTA being determined by titration with a standard solution of lead nitrate; the total lead-plus-tin content of the solution is thus determined. Sodium fluoride is then added and this displaces the EDTA from the tin (IV)-EDTA complex; the liberated EDTA is determined by titration with a standard lead solution.

**Procedure:-**

**1.** Prepare a standard EDTA solution (0.2M), a standard lead solution (0.01 M), a 30 per cent aqueous solution of hexamine, and a 0.2 per cent aqueous solution of xylenol orange.

**2.** Dissolve a weighed amount (about 0.4 g) of solder in 10 mL of concentrated hydrochloric acid and 2 mL of concentrated nitric acid; gentle warming is necessary.

**3.** Boil the solution gently for about 5 minutes to expel nitrous fumes and chlorine, and allow cooling slightly, whereupon some lead chloride may separate.

**4.** Add 25.0 mL of standard 0.2M EDTA and boil for 1 minute; the lead chloride dissolves and a clear solution is obtained. Dilute with 100 mL of de-ionized water, cool and dilute to 250 mL in a graduated flask.

**5.** Without delay, pipette two or three 25.0 mL portions into separate conical flasks. To each flask add l5mL hexamine solution, ll0 mL de-ionized water, and a few drops of xylenol orange indicator.

**6.** Titrate with the standard lead nitrate solution until the color changes from yellow to red.

**7.** Now add 2.0 g sodium fluoride; the solution acquires a yellow color owing to the liberation of EDTA from its tin complex.

**8.** Titrate again with the standard lead nitrate solution until a permanent (i.e. stable for 1 minute) red color is obtained. Add the titrant drop wise near the end point; a temporary pink or red color gradually reverting to yellow signals the approach of the end point.

**Calculation**:-

$$\text{mmol of ( Sn + Pb)} = \text{mmol EDTA- mmol } Pb(NO_3)_2$$

$$\text{mmol of Pb} = \text{nnol EDTA - mmol Sn}$$

$$\text{mmol of Sn} = \text{mmol of (Sn + Pb) - mmol of Pb}$$

$$\text{mmol Pb} = \frac{\text{Wt. Pb}}{\text{A.Wt.}} * 1000$$

$$\text{\% Pb in mixture} = \frac{\text{Wt. Pb}}{\text{Wt. sample}} * 100$$

$$\text{mmol Sn} = \frac{\text{Wt. Sn}}{\text{A. Wt.}} * 1000$$

$$\text{\% Sn in mixture} = \frac{\text{Wt. Sn}}{\text{Wt. sample}} * 100$$

**Discussion:-**

1. Why NaF is added?
2. What displacement reaction (or titration)?
3. What is the solder? And what is contained?
4. Why is the $HNO_3$ and HCl solution are added?
5. Why hexamine is added and xylenol organic indicator?

## Experiment No.(37):-Determination of silver : indirect method

**Theory:-**Silver halides can be dissolved in a solution of potassium tetracyanonickelate(II) in the presence of an ammonia—ammonium chloride buffer, and the nickel ion set free may be titrated with standard EDTA using murexide as indicator.

$$2Ag^{+} + [Ni(CN)_4]^{+2} = 2[Ag(CN)_2]^{-} + Ni^{+2}$$

It can be shown from a consideration of the overall stability constants of the ions $[Ni(CN)_4]^{+2}$ ($10^{27}$) and $[Ag(CN)_2]^{-}$ ($10^{21}$) that the equilibrium constant for the above ionic reaction is $10^{15}$, i.e. the reaction proceeds practically completely to the right. An interesting exercise is the analysis of a solid silver halide, e.g. silver chloride.

**Procedure:-**

1. Prepare the indicator by grinding 0.1 g murexide with l0g of potassium nitrate; use about 50 mg of the mixture for each titration.

2. And an ammonium chloride solution (1 M) by dissolving 26.75 g ammonium chloride in de-ionized water in a 500 mL graduated flask.

3. The potassium tetracyanonickelate(II) which is required to be prepared as follows. Dissolve 25 g of analytical grade $NiSO_4.7H_2O$ in 50 mL distilled water and add portion wise, with agitation, 25g potassium cyanide. (Caution: use a fume cupboard.) A yellow solution forms and a white precipitate of potassium sulphate separates.

4. Gradually add, with stirring, 100 mL of 95 per cent ethanol, filter off the precipitated potassium sulphate with suction, and wash twice with 2 mL ethanol.

5. Concentrate the filtrate at ‘about 70 °C an infrared heater is convenient for this purpose. When crystals commence to separate, stir frequently. When the crystalline mass becomes thick (without evaporating completely to dryness), allow cooling and mixing the crystals with 50 mL ethanol. Separate the crystals by suction filtration and wash twice with 5 mL portions ethanol. Spread the fine yellow crystals in thin layers upon absorbent paper, and allow standing for 2-3 days in the air, adequately protected from dust. During this period the excess of potassium cyanide is converted into potassium carbonate. The preparation is then ready for use; it should be kept in a stoppered bottle.

6. Treat an aqueous suspension of about 0.072 g (accurately weighed) silver chloride with a mixture of 10 mL of concentrated ammonia solution and 10 mL of 1 M ammonium chloride solution, then add about 0.2 g of potassium cyanonickelate and warm gently. Dilute to 100 mL with de-ionized water, add 50 mg of the indicator mixture and titrate with standard (0.01M) EDTA solution, adding the reagent drop wise in the neighborhood of the end point, until the color changes from yellow to violet.

7. Palladium (II) compounds can be determined by a similar procedure, but in this case, after addition of the cyanonickelate, excess of standard (0.01 M) EDTA solution is added, and the excess is back-titrated with standard (0.01M) manganese (II) sulphate solution using solochrome black indicator. Gold may be titrated similarly.

**Calculation:-**

$$\text{mmo, Ag+} = \text{mmol EDTA} * \frac{\text{mole Ag}^+}{\text{mole EDTA}}$$

$$\frac{\text{Wt.}}{\text{A.Wt}} * 1000 = (M * V) * \frac{2}{1}$$

$$\% \text{ Ag} = \frac{\text{Wt.}}{\text{Wt. sample}} * 100$$

**Discussion:-**

1. Why ethanol is added?
2. What is the yellow perception?
3. Why $NH_4Cl$, $NiSO_4.7H_2O$, and KCN are added?
4. Write chemical equation to express the titration reaction?

## Experiment No.(38):- Determination of Protein in Bread

**Theory:-**This quantitative method of analysis for proteins is based on a determination of the %w/w N in the sample. Since different cereal proteins have similar amounts of nitrogen, the experimentally determined %w/w N is multiplied by a factor of 5.7 to give the %w/w protein in the sample (on average there are 5.7 g of cereal protein for every gram of nitrogen). As described here, nitrogen is determined by the Kjeldahl method. The protein in a sample of bread is oxidized in hot concentrated $H_2SO_4$, converting the nitrogen to $NH_4^+$. After making the solution alkaline, converting $NH_4^+$ to $NH_3$, the ammonia is distilled into a flask containing a known amount of standard strong acid. Finally, the excess strong acid is determined by a back titration with a standard strong base titrant.

**Procedure:-**

1. Transfer a 2.0-g sample of bread, which has previously been air dried and ground into a powder.
2. To a suitable digestion flask, along with 0.7 g of HgO as a catalyst, 10 g of $K_2SO_4$, and 25 mL of concentrated $H_2SO_4$. Bring the solution to a boil, and continue boiling until the solution turns clear, and for at least an additional 30 min.
3. After cooling to below room temperature, add 200 mL of $H_2O$ and 25 mL of 4% w/v $K_2S$ to remove the $Hg^{2+}$ catalyst. Add a few Zn granules to serve as boiling stones, and 25 g of NaOH.
4. Quickly connect the flask to a distillation apparatus, and distill the $NH_3$ into a collecting flask containing a known amount of standardized HCl. The tip of the condenser should be placed below the surface of the strong acid.
5. After the distillation is complete, titrate the excess strong acid with a standard solution of NaOH, using methyl red as a visual indicator.

**Calculation:-**

**Discussion:-**

1. Oxidizing the protein converts the nitrogen to $NH_4^+$. Why is the amount of nitrogen not determined by titrating the $NH_4^+$ with a strong base?
2. Ammonia is a volatile compound as evidenced by the strong smell of even dilute solutions. This volatility presents a possible source of determinate error. Will this determinate error be negative or positive?
3. Discuss the steps taken in this procedure to minimize this determinate error?
4. How does K2S remove $Hg^{2+}$, and why is this important?

## Experiment No.(39):- Determination of Total Chlorine Residual

**Theory:-**The chlorination of public water supplies results in the formation of several chlorine-containing species, the combined concentration of which is called the total chlorine residual. Chlorine may be present in a variety of states including free residual chlorine, consisting of $Cl_2$, HOCl, and $OCl^-$, and combined chlorine residual, consisting of $NH_2Cl$, $NHCl_2$, and $NCl_3$. The total chlorine residual is determined by using the oxidizing power of chlorine to convert $I^-$ to $I_3^-$.

The amount of $I_3^-$ formed is then determined by a redox titration using $S_2O_3^{2-}$ as a titrant and starch as an indicator. Regardless of its form, the total chlorine residual is calculated as if all the chlorine were available as $Cl_2$, and is reported as parts per million of Cl.

**Procedure:-**

**1.** Select a volume of sample requiring less than 20 mL of $S_2O_3^{2-}$ to reach the end point.

2. Using glacial acetic acid, acidify the sample to a pH in the range of 3 to 4.
3. Add about 1 g of KI. And titrate with $Na_2S_2O_3$ until the yellow color due to $I_3^-$ begins to disappear.
4. Add 1 mL of a starch indicator solution, and continue titrating until the blue color of the starch–$I_3^-$ complex disappears. The volume of titrant needed to reach the end point should be corrected for reagent impurities by conducting a blank titration.

**Calculation:-**

**Discussion:-**

1. Is this an example of a direct or an indirect analysis?
2. Why is the procedure not carried out directly using KI as a titrant?
3. Both oxidizing and reducing agents can interfere with this analysis. Explain what effect each of these interferes will have on the result of an analysis?



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# التحليل الكيميائي الحجمي العملي

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