Ministry 0f Higher Education and scientific Research

Al-Mustansiriya University

Collage of Science

Department of Chemistry

Practice Volumetric Chemical Analysis

First year / 2020

Edited by
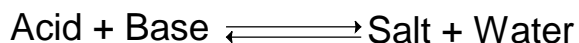
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1//Acid–base titration تسحيح حامض ــقاعدة:-

It is acid react with base to obtain salt and water:-

Acid + Base ⇌ 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	pH	Indicator color	
		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

تسحيح ومعايرة حامض الهايدروكلوريك

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

$$M * V \textbf{ ml} \quad = 0.1 * 50 \textbf{ ml}$$

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$_2$CO$_3$ 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 M of HCl:-

m mol HCl = m mol Na_2CO_3

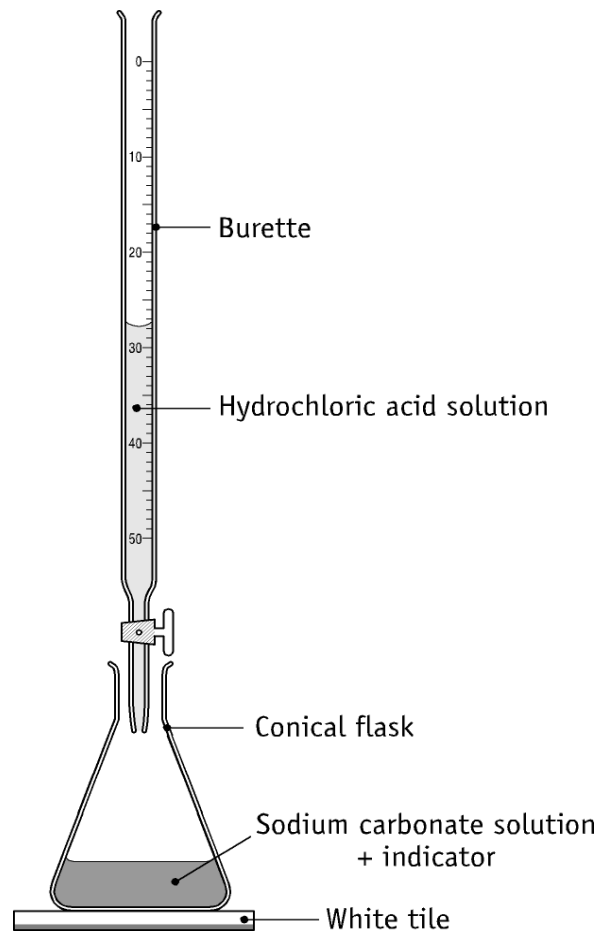$(M * V)$ HCl = $(M * V)$ Na_2CO_3 * $\frac{1}{2}$

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

Discussion المناقشة:-

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?

Burette

Hydrochloric acid solution

Conical flask

Sodium carbonate solution + indicator

White tile

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

تسحيح ومعايرة هيدروكسيد الصوديوم

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:-

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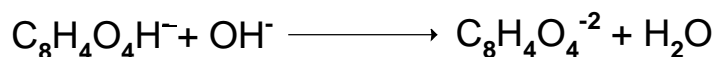
Procedure:-

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

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

Wt. = N* Eq.Wt * 0.05

= 0.1 * 204 * 0.05

= 1.02 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 :-

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

Wt. = N* Eq.Wt * 0.05

= 0.1 * 40 * 0.05

= 0.2 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:-

$$meq. \ NaOH = meq \ KHP$$

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

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

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

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

Discussion المناقشة:-

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?

Complex –formation Titration تسحيحات تكوين معقدات:-

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.

$$M^{+n} + \ _nL \ \rightleftharpoons \ MLn$$

metal   **ligand**   **complex**

$$Ag^+ + :NH_3 \rightleftharpoons Ag(NH_3)^+$$
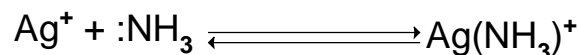
The **coordination number** of a cation is the number of covalent bonds that a cation tends to form with electron donor groups.Titrimetric methods based upon complex formation.A ligand that has more than two donor group chelating agents are known. Like EDTA (Ethylene di amine tetra acetic acid)

$$HOOCH_2C \diagdown \diagup CH_2COOH$$
$$NCH_2CH_2N$$
$$HOOCH_2C \diagup \diagdown CH_2COOH$$
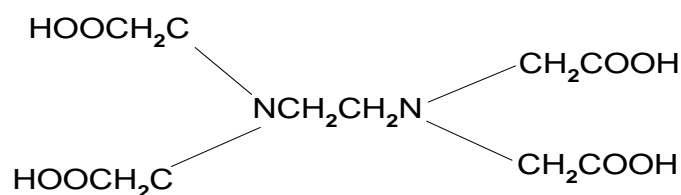
The use of a metal ion indicator in an EDTA titration may be written as:

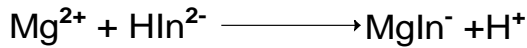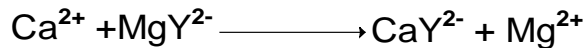$$M\text{-}In + EDTA \; = \; M\text{-}EDTA + In$$
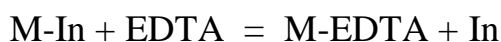
This reaction will proceed if the metal-indicator complex M-In is less stable than the metal-EDTA complex M-EDTA. The former dissociates to a limited extent, and during the titration the free metal ions are progressively complexed by the EDTA until ultimately the metal is displaced from the complex M-In 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.(3):- Determination of water hardness تقدير عسرة الماء

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:-

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

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, <mark>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.</mark> 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:-

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

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

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

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 المناقشة:-

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?

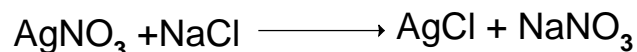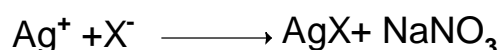## // *Precipitation titration* التسحيح الترسيبي:-

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.(4):- Preparation and standardization of 0.1 N $AgNO_3$ solution with sodium chloride (Mohr Method)

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تسحيح ومعايرة نترات الفضه (طريقة مور)

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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^-:-

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

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

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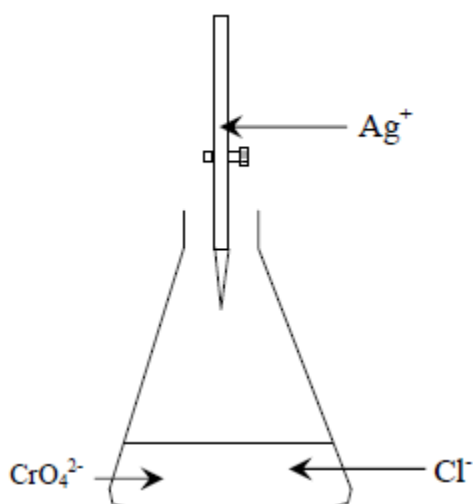
Discussion:-

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.(5):- Determination of Chloride by Fajan's method (Adsorption indictors)

تسحيح ومعايرة نترات الفضة (طريقة فايان)(دلائل الامتزاز)

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.

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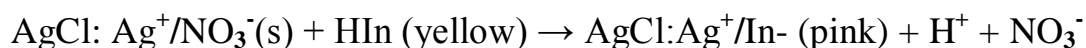
Procedure:-

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:-

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

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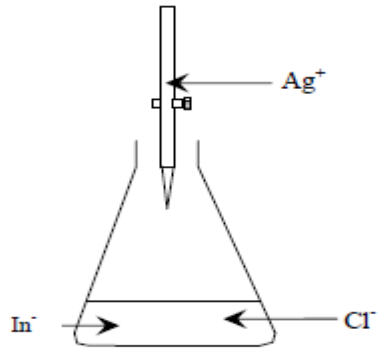
Discussion:-

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?