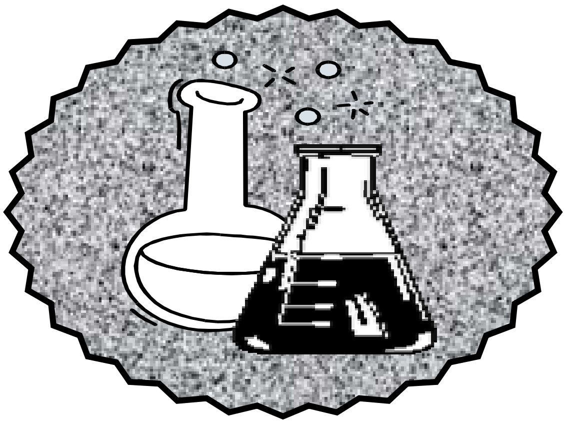
FIRST YEAR



Practical Analytical Chemistry

(2nd term)

Safety and Laboratory Rules

1- You will not perform special experiments or any procedure, except the one assigned to you.

2- Read the label on a reagent bottle twice before removing any chemicals. The wrong chemicals can lead to accidents or unexplainable results in experiments.

3- When you are not sure about the label on a bottle or which chemical to use, ask the instructor. You will not guess and you will not ask another student.

4- Bottles should never be grasped by the neck but should be held firmly around the body.

5- Do not take more than the necessary amount of any solution or reagent and do not return excess chemicals to the reagent bottles.

6- When heating anything in a test tube, you will point the tube mouth along the length of the bench and will be sure not to point it at any person.

7- When diluting acid, you will pour the acid into the water.

8- If an acid or corrosive chemical is spilled on your skin, Wash it off immediately with plenty of cold water, and consult your instructor.

9- To protect your clothing from corrosive chemicals, always wear a laboratory coat.

10- The girls must tie their hair and take off all accessories.

11- Never taste, smell or touch a chemical or solution unless specifically directed to do so.

12- When smelling a substance, you will use your hand to wave the vapors toward your face.

13- Chemicals, which have poisonous or unpleasant vapors, should be used in the fume hood, when irritating or toxic gases are produced by the experiment you are working on, you will move the whole experiment into the hood and turn on the fan.

14- It is desirable to wear protective glasses during laboratory work, because the eyes are particularly susceptible to permanent damage by corrosive chemicals as well as by flying fragments.

15- If a chemical is splashed in your eye accidentally, you will have someone immediately wash your eye with running water. You will have to continue to wash out your eye for twenty minutes.

16- Do not wear contact lenses in the laboratory.

17- Always wash your face, hands and arms before leaving the laboratory.

18- Make sure that the gas and water taps are turned off before you leave the laboratory.

19- Students are asked to keep their desks, glassware and other laboratory tools clean and dry.

20- Discard used paper products such as litmus paper, filter paper, broken glass and matches into wastebasket. The sink is not the disposable for everything.

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1ST SECTION (PART I)

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Classification of Analytical Chemistry

Analytical Chemistry

- **Qualitative Analysis** (=What?) معرفة نوع المادة
  - **Analysis of Anions**
  - **Analysis of Cations**
- **Quantitative Analysis** *or* **Determination** *or* **Estimation** *or* **Assay** (=How much?) معرفة كمية أو تركيز المادة
  - **Volumetric Analysis (Titration)** يعتمد على قياس الحجم
    - **Acid-base titration** (Aqueous & Non-aqueous)
    - **Precipitation titration** ⇐
    - **Complex-formation titration** ⇐
    - **Redox titration**
  - **Gravimetric Analysis** ⇐ يعتمد على قياس الوزن
  - **Instrumental Analysis** يعتمد على التحليل بالأجهزة

The most important application in pharmaceutical industry

Precipitation Titration
(= Precipitimetric Titration)
(= Precipitate-formation Titration)

Introduction:

⇒ **Definition of Precipitation Titration:**

It is a type of volumetric analysis that depends on the formation of a precipitate.

⇒ The most important precipitating agent used in precipitation titration is **Silver Nitrate ($AgNO_3$)**.

⇒ Titrimetric methods based upon using silver nitrate ($AgNO_3$) are called **Argentometric titration.**

⇒ Argentometric titrations are mainly used for determination of halides (Cl^-, Br^- & I^-). It is also used for the determination of SCN^-, CN^- and some compounds that form insoluble products (ppt) with $AgNO_3$.

Types of Precipitation Titration:

Precipitation titrations are classified into 3 main types according to the method of detection of end point:

1. **Volhard's method** ⇒ depends on the formation of **Colored complex ions (Colored solution).** تغييرفي لون المحلول
2. **Fajan's method** ⇒ depends on the formation of **Colored adsorption compound.** تغييرفي لون الراسب
3. **Mohr's method** ⇒ depends on the formation of **Colored 2ry precipitate.** تكوين راسب جديد ملون

Mohr's Method

It is a type of precipitation titration that depends on the formation of a colored 2ry ppt at the end point.

Main features of Mohr's method:

• **Sample:**	Cl^- , Br^- (Not for I^- or SCN^-).
• **Type of titration:**	Direct titration.
• **Standard Solution:**	Standard $AgNO_3$.
• **pH:**	Neutral or slightly alkaline. (pH ≈6.5 -9).
• **Indicator:**	1 ml of 5% Pot. Chromate (K_2CrO_4) soln.
• **Color at E.P.:**	1st permanent darkening of the yellow chromate color [due to the formation of Ag_2CrO_4 (brick red ppt) at the end point leading to darkening of the soln.].

Exp.(1): Determination of NaCl by Mohr's method

Principle :

It depends on the titration of NaCl sample with standard $AgNO_3$ using potassium chromate (K_2CrO_4) as indicator.

Titration reaction:

$$\underset{\text{sample}}{Cl^-} + \underset{\text{titrant}}{Ag^+} \rightarrow \underset{\text{white ppt}}{AgCl\downarrow}$$

End point reaction:

$$\underset{\text{titrant}}{2\,Ag^+} + \underset{\text{indicator}}{CrO_4^{--}} \rightarrow \underset{\text{brick red ppt}}{Ag_2CrO_4\downarrow}$$

In this experiment, Cl^- sample is titrated with Ag^+ in presence of CrO_4^{--} indicator where AgCl is precipitated as a white ppt before Ag_2CrO_4 THEN at the end point (i.e. when Cl^- is completely reacted with Ag^+), the first slight excess of Ag^+ will react with CrO_4^{--} indicator giving Ag_2CrO_4 (brick red ppt) leading to darkening of the yellow color of the soln.

Notes:

1) **Effect of pH**: Mohr's method should be done in neutral or slightly alkaline medium (pH ≈6.5 -9) because:

   At pH > 9: Ag^+ will be precipitated as AgOH↓ (brown to black ppt) leading to Consumption of the titrant & Masking of the E.P. color.

   $$Ag^+ + OH^- \rightarrow AgOH\downarrow \textit{ (brown to black ppt)}$$

   While at pH < 6.5: The chromate ion (CrO_4^{--}) changes into acid chromate ($HCrO_4^-$) then to dichromate ($Cr_2O_7^{--}$). Both $HCrO_4^-$ & $Cr_2O_7^{--}$ form soluble salts with Ag^+ & so no colored ppt will be formed at the E.P.

   $$\underset{\text{chromate}}{2\,CrO_4^{--}} + 2\,H^+ \rightarrow \underset{\text{acid chromate}}{2\,HCrO_4^-} \rightarrow \underset{\text{dichromate}}{Cr_2O_7^{--}} + H_2O$$

2) Ag_2CrO_4 is more soluble than AgCl so that No Ag_2CrO_4 will be precipitated until all Cl^- ions have been precipitated as AgCl provided that the CrO_4^{--} concentration should be adjusted to make Ag_2CrO_4 formed only at the end point and so prevent error in the end point. 1 ml of 5% K_2CrO_4 solution is suitable.

   High concentration of K_2CrO_4 $\Rightarrow$ gives too soon (early) E.P.
   because Ag_2CrO_4 will be rapidly precipitated before E.P.

   Low concentration of K_2CrO_4 $\Rightarrow$ gives too late E.P.
   because CrO_4^{--} will be insufficient and so a large amount of Ag^+ (titrant) will be needed to precipitate Ag_2CrO_4 and so the E.P. comes too late.

3) I^- & SCN^- can not be determined by Mohr's method because the formed AgI & AgSCN strongly adsorb CrO_4^{--} on their surfaces and so the ppt formed at the end point will be an adsorption compound which is less colored and so less sharp E.P. will be obtained.

4) BLANK EXPERIMENT should be done because: An additional excess of $AgNO_3$ (titrant) will be added after the correct E.P. to form enough Ag_2CrO_4 to be seen over the heavy white ppt of AgCl & the yellow color of K_2CrO_4 indicator leading to error (increase) in the end point. This error can be corrected by performing **blank determination** to know the volume of the additional excess of $AgNO_3$ (titrant) that causes error.

   In **blank determination**, all steps of the experiment are performed in absence of sample but using 10 ml dist. water instead of it and also using talc or $CaCO_3$ powder to imitate (تحاكي) the white AgCl ppt.

   i.e. 10 ml dist. water + 1 ml 5% K_2CrO_4 + talc or $CaCO_3$ powder $\rightarrow$ titate $\neq$ st. $AgNO_3$ till the 1st darkening of the yellow chromate color.

   The volume consumed of $AgNO_3$ (titrant) is called **Indicator Blank** and it should be subtracted from the observed E.P. in the original experiment {i.e. the calculation of concn. involves (E.P. - Ind. Blank)}.

Procedure :

(Refer to Instructions For Using Glassware in the 1st term course)

1) Transfer 10 ml of the sample into a clean conical flask.

2) Add 1 ml of 5% K_2CrO_4 indicator *(by graduated pipette)*.

3) Titrate ≠ 0.01 N $AgNO_3$

{ Color at E.P.: 1st permanent darkening of the yellow chromate color **}**

Before starting tit.: Cl^- sample + CrO_4^{--} ind. ⇒ Clear bright yellow soln.

(colorless) ***(yellow color)***

During tit. ≠ $AgNO_3$: $AgCl\downarrow$ + Cl^- sample + CrO_4^{--} ind. ⇒ Turbid bright yellow soln.

(white ppt) ***(colorless)*** ***(yellow color)***

At the end point: $AgCl\downarrow$ + CrO_4^{--} ind. + *few* $Ag_2CrO_4\downarrow$ ⇒ Turbid dark yellow soln.

(white ppt) ***(yellow color)*** ***(brick red ppt)***

Calculations :

(Refer to Calculations for Titrations in the 1st term course, p. 1-10)

Calculations in precipitation titrations differ from that in acid-base titration in the calculation of equivalence factor where (**b**) in precipitation titration equals the number of univalent cation atoms present in or equivalent to ONE molecule of the standard.

In other words, (**b**) equals the total positive charge on the cation radical of ONE molecule of the standard.

ex.: For $\overset{+1}{\mathbf{Ag}}\vdots\mathbf{NO_3} \Rightarrow b = 1$, For $\overset{+1}{\mathbf{NH_4}}\vdots\mathbf{SCN} \Rightarrow b = 1$, For $\overset{+2}{\mathbf{Hg}}\vdots\mathbf{(NO_3)_2} \Rightarrow b = 2$

For this experiment:

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

$$\therefore \underset{standard}{1\ AgNO_3} \equiv \underset{sample}{1\ NaCl}$$

Equivalence factor (F):

$$\text{each ml of 0.01 N } AgNO_3 \equiv \frac{1 \times \text{M.W. of NaCl} \times 0.01}{1 \times 1000} \equiv \text{.......... g NaCl}$$

Concentration:

$$\text{Concn. of NaCl} = \frac{(\text{E.P.- Ind. blank}) \times F \times 1000}{10} = \text{.......... g/L}$$

Exp.(2): Determination of NaBr by Mohr's method

The **Principle**, **Procedure** and **Calculations** for **NaBr** are in the same manner as **NaCl** except that: The formed ppt is **AgBr↓** which a **yellowish white ppt**.

$$\underset{sample}{Br^-} + \underset{titrant}{Ag^+} \rightarrow \underset{\text{Yellowish white ppt}}{AgBr\downarrow}$$

✽✽✽✽✽ >>*Best wishes* >> ✽✽✽✽✽