

# Gravimetric Analysis



**Mrs. Jigna T. Patel** M.Pharm., Ph.D. (Pursuing)

*Assistant Professor*

*Department of Pharmaceutical Analysis and Pharmaceutical Chemistry*

*Saraswati Institute of Pharmaceutical Sciences*

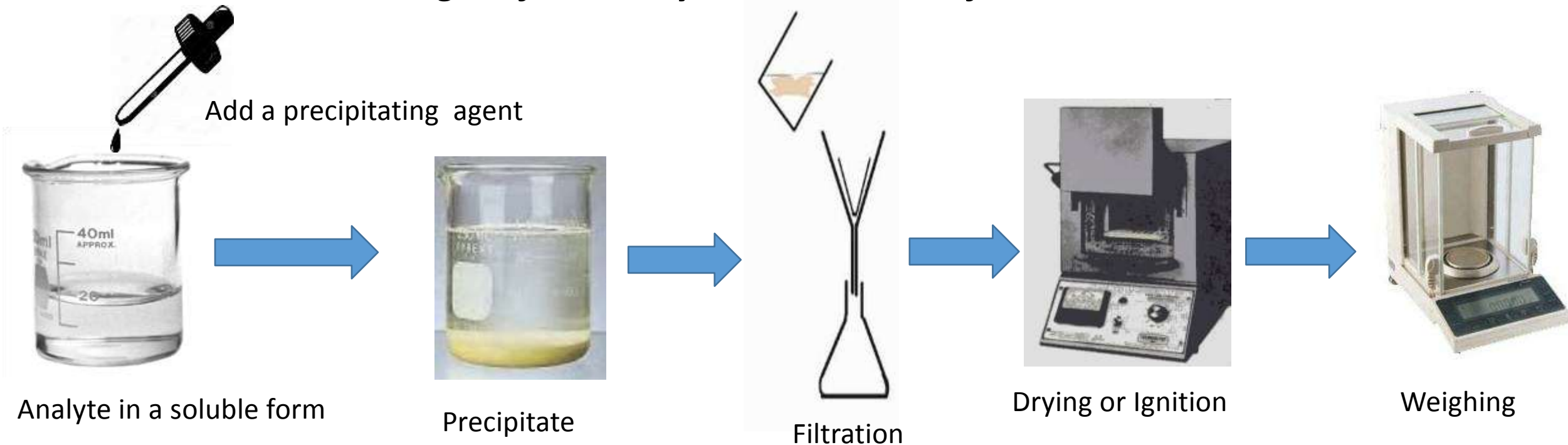
*At. & Po.: Dhanap, Gandhinagar, Gujarat, India - 382355*

# Learning Outcomes

- Mention the main steps of **gravimetric analysis**.
- Define **supersaturation**.
- Identify types of **impurities** in precipitates.
- Define **peptization**.
- Define **gravimetric factor**.
- Apply **gravimetric analysis** to different samples.

# Gravimetric analysis

- Gravimetric analysis is one of the most accurate and precise methods of **macro-quantitative analysis**.
- The **analyte** is selectively converted into an **insoluble form (precipitate)**.
- The separated precipitate is then **dried or ignited**, possibly to another form and is **accurately weighed**.
- From the weight of the precipitate and knowledge of its chemical composition, we *can calculate the weight of the analyte in the desired form.*



# Properties of the Precipitate

The ideal product (precipitate) of a gravimetric analysis should be:

- Sufficiently insoluble (the precipitate is of such low solubility that losses from dissolution are negligible)
- Easily filterable (crystals of large particle size so as not to pass through the filtering system).
- Very pure (less possibility that the precipitates carry some of the other constituents of the solution with them).
- Should possess a known composition (known chemical structure).

# Steps of Gravimetric Analysis

1

- Precipitation

2

- Digestion

3

- Filtration

4

- Washing

5

- Drying or Ignition

6

- Weighing

7

- Calculations

# 1. Mechanism of Precipitation

➤ When a solution of precipitating agent is added to a test solution to form a precipitate, such as in the addition of  $\text{AgNO}_3$  to a chloride solution to precipitate  $\text{AgCl}$ .

The actual precipitation occurs in a series of steps:

## 1. Super Saturation

Ionic product > Solubility product

Unstable state: solution contains a lot of dissolved ions more than it can accommodate.

To become stable: Precipitation takes place.

## 2. Nucleation

A minimum number of particles come together to produce microscopic nuclei of the solid phase.

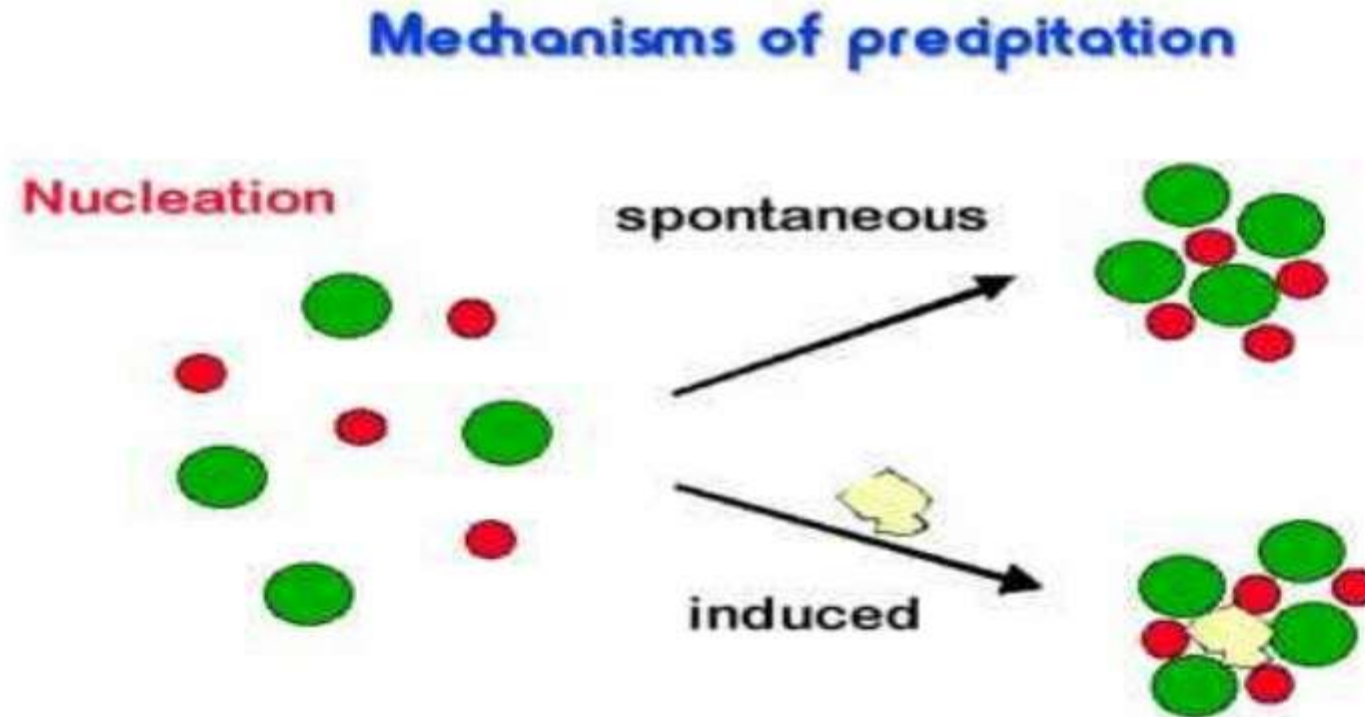


## 3. Particle Growth

Nuclei join together to form a crystal of a certain geometric shape



# 1- Mechanism of Precipitation (cont.)



Spontaneous nucleation will occur on its own.

Induced nucleation requires a 'seed' particle to get things started (dust, another crystal, glass fragment, ...)

# 1- Mechanism of Precipitation (cont.)

## Mechanisms of precipitation

### Particle growth



Once a nucleation site has formed, other ions are attracted to the site. This will result in the formation of large, filterable particles.

If done properly, it also reduces contaminants since they don't 'fit in' to the crystal structure.

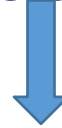


# 1- Mechanism of Precipitation (cont.)

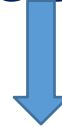
## Important Notes

When a solution is supersaturated, **it is in an unstable state** and this favors rapid nucleation to form a large number of small particles.

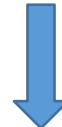
A higher degree of supersaturation



A greater rate of nucleation



A greater number of nuclei formed per unit time



Precipitate is in the form of a large number of small nuclei



Increase total surface area of precipitate which increases the possibility of entrapment of impurities



Precipitate is not of filterable size



# 1- Mechanism of Precipitation (cont.)

## Degree of supersaturation

**Von Weimarn** discovered that the particles size of precipitates is inversely proportional to the relative supersaturation of the solution during the precipitation process

Relative supersaturation = 
$$\frac{Q - S}{S}$$

**Q** is the concentration of the solute at any instant.

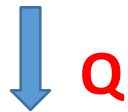
**S** is its equilibrium solubility.

**HIGH RSS**  **Many small crystals (Large Surface Area)**

**Low RSS**  **Fewer large crystals (Small Surface Area)**

Low RSS is favorable.  
How to achieve it?

**During precipitation:**



# 1- Mechanism of Precipitation (cont.)

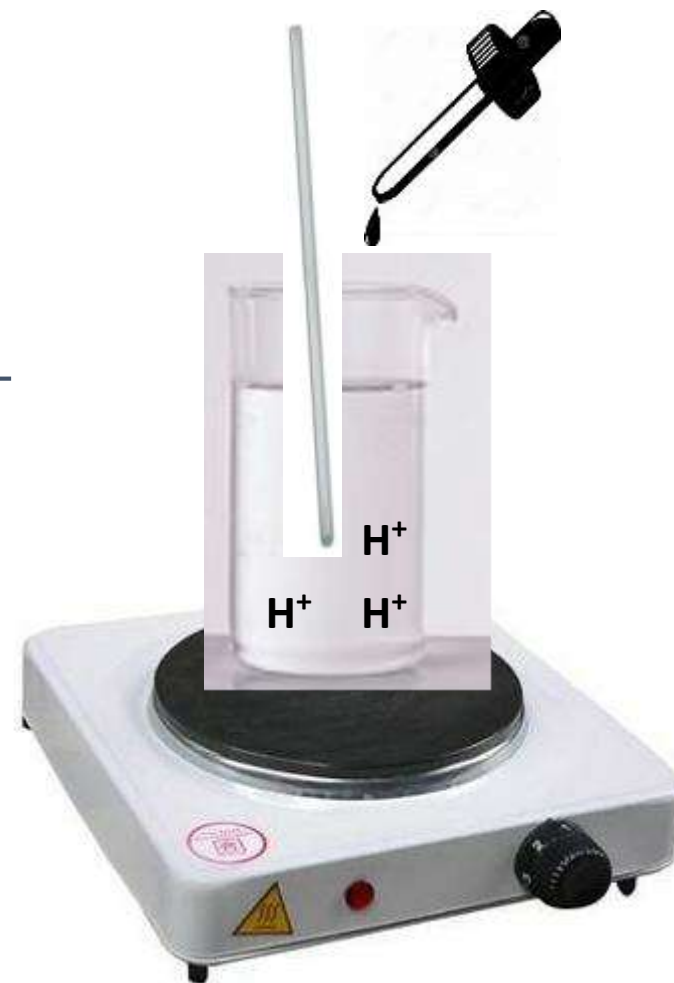
Favorable conditions for precipitation

## To decrease the value of $Q$

- Precipitate from dilute solutions.
- Add dilute precipitating agents slowly with constant stirring.

## To increase the value of $S$

- Precipitate from hot solution.
- Precipitate at as low pH as possible.



## 2. Digestion

- Digestion is keeping the precipitate formed in contact with the **mother liquor** for a specified amount of time.

**Mother liquor** (the solution from which it was precipitated).

**In case of Colloidal precipitates:**

Particle size (less than  $100 \text{ }\mu\text{m}$ )

Digestion is performed by allowing the precipitate to remain in contact with the mother liquor at high temperature for a couple of hours.

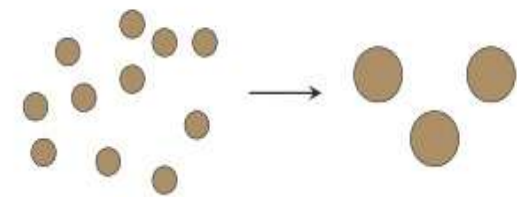
**In case of Crystalline precipitates:**

Particle size (more than  $100 \text{ }\mu\text{m}$ )

Digestion is performed by allowing the precipitate to remain in contact with the mother liquor for a long time.

### **Why is it important?**

- 1- The small particles tend to dissolve and re-precipitate on the surfaces of large crystal.
- 2- Individual particles tend to agglomerate together.
- 3- Imperfections of the crystals tend to disappear and adsorbed or trapped impurities tend to escape into solution.



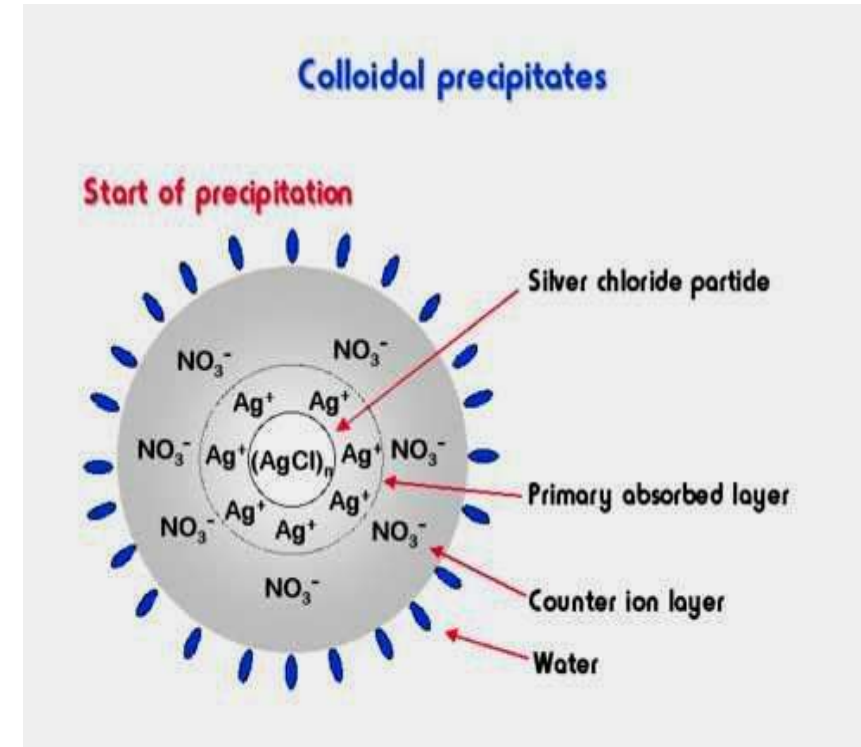
## 2. Digestion Cont.

### For colloidal precipitate

- The surface of the precipitate tends to adsorb the ion of the precipitated particle that is in excess in the solution, ( $\text{Ag}^+$  or  $\text{Cl}^-$ ).
- This primary adsorbed layer attracts oppositely charged ion in a secondary or counter layer **(they are less tightly held than the primary adsorbed ion)**.
- The negatively charged ionic atmosphere of the particles repel one another leading to the colloidal state.

### **How does digestion help solve this problem?**

- The colloidal particles, therefore, must have enough kinetic energy to overcome electrostatic repulsion before they can coalesce.
- Thus, digestion at high temperature increases the colloidal particles' kinetic energies and can promote coalescence (coagulation).



# Impurities encountered in Gravimetric Analysis

- **1. Occlusion**

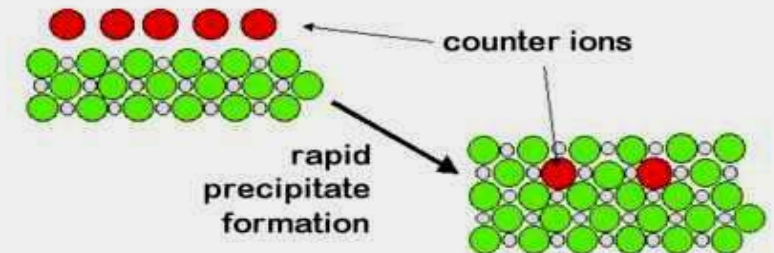
- This occurs when materials that are not part of the crystal structure are trapped within the crystal.
- **For example**, water or any counter ion can be occluded in any precipitate.
- This causes **deformation in the crystal.**
- This type is hard to be removed, **digestion can decrease it to a certain extent.**



## Occlusion and entrapment

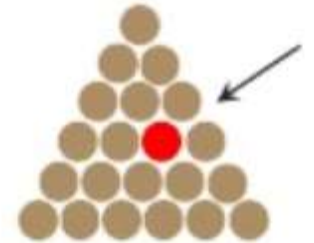
### Occlusion

If crystal growth is too rapid, some counter ions don't have time to escape from the surface.



# Impurities encountered in Gravimetric Analysis

- **2. Inclusion (isomorphous replacement)**
- This occurs when a compound that is **isomorphous** to the precipitate is entrapped within the crystal.
- **Isomorphous** means they have the same type of formula and crystals in similar geometric form.
- This type of impurity doesn't lead to deformation of the crystals.
- **Example**,  $K^+$  has nearly the same size of  $NH_4^+$  so it can replace it in Magnesium ammonium phosphate.
- Digestion **cannot handle this type and mixed crystals will be formed.**



# Impurities encountered in Gravimetric Analysis

- **3. Surface adsorption**

- Surface adsorption is very common especially in colloidal precipitates.
- Example, AgCl, BaSO<sub>4</sub> where each of them will have a primary adsorption layer of the lattice ion present in excess followed by a secondary layer of the counter ion of opposite charge.
- These adsorbed layers can often be removed by washing where they can be replaced by ions that can be easily volatilized at the high temperature of drying or ignition.

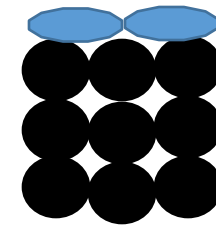
~~Adsorbed, occluded and included impurities~~ are said to be **coprecipitated**.  
That is, impurity is precipitated along with the desired product during its formation.



# Impurities encountered in Gravimetric Analysis

- **4. Post precipitation**

- When the precipitate is allowed to stand in contact with the mother liquor, a second substance will slowly form a precipitate on the surface of the original one.
- **Examples**, When calcium oxalate is precipitated in the presence of magnesium ions, magnesium oxalate may be if the solution is left without filtration for a long time.
- Digestion will increase the extent of such type, dissolution and reprecipitation will decrease the extent of post precipitation.



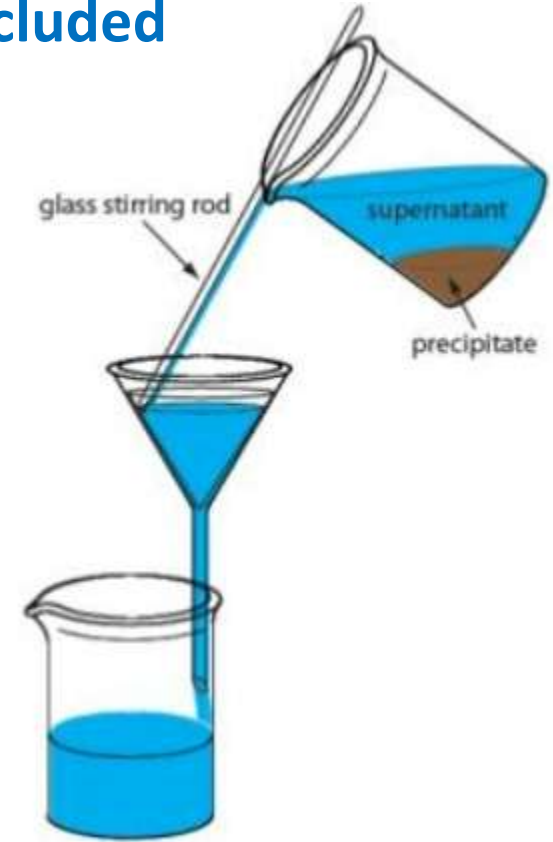
# 3- Filtration and Washing of the Precipitate

➤ Washing helps remove the **co-precipitated impurities** specially the **occluded** and **surface adsorbed**.

➤ The precipitate will also be **wet with the mother liquor** which is also removed by washing.

**Note that:**

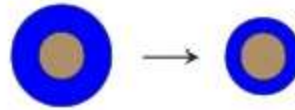
➤ Colloidal precipitates can not be washed with pure water, because **peptization** occurs. This is the **reverse of coagulation**.



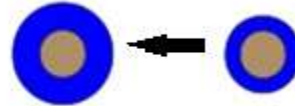
# 3,4- Filtration and Washing of the Precipitate

## Peptization

- As we said before that colloidal precipitates **have double layer of adsorbed primary and counter ions**.
- The presence of **another electrolyte** during precipitation will cause the **counter ions** to be **forced into closer contact with primary layer**, thus promoting coagulation.



- **Washing with water** will dilute and remove foreign ions and the counter ion will occupy a larger volume, with more solvent molecules between it and the primary layer.



- This can be prevented **by adding an electrolyte to the washing liquid**. e.g.  $\text{HNO}_3$  is used to wash  $\text{AgCl}$ .
- This **electrolyte** should be **volatile** at the temperature of **drying or ignition** and must **not dissolve the precipitate**.

## 5- Drying or Ignition



**Ashless filter paper**



**Porcelain crucible**  
**(Ignition up to 1000 °C)**



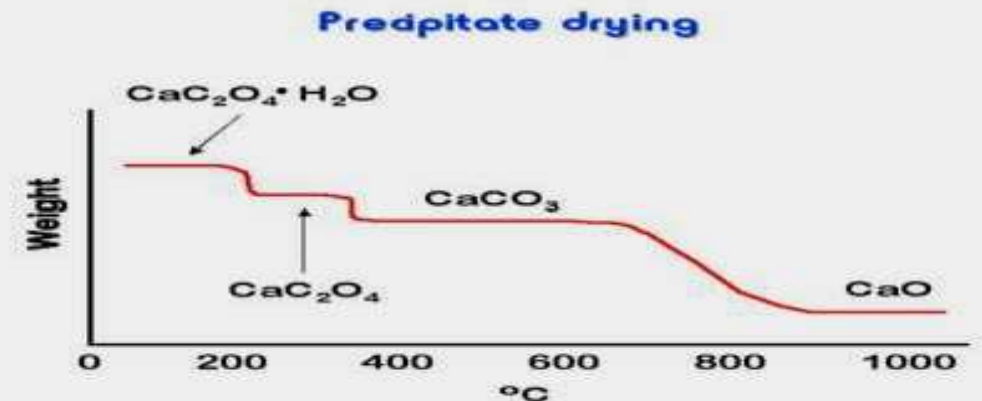
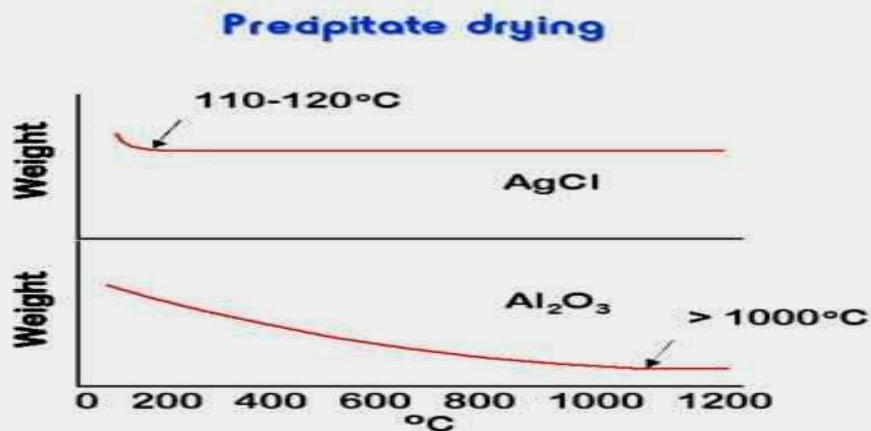
**Glass crucible**  
**(Drying at 100-120 °C)**

# 5- Drying or Ignition

- After filtration, a gravimetric precipitate is heated until its mass becomes constant.
- **Drying** at **110 to 120 °C** for 1-2 hours is conducted If the collected **precipitate** is in a form suitable for weighing (**known, stable composition**), it must be heated to **remove water** and to **remove adsorbed electrolyte from the wash liquid**.
- **Ignition** (strong heating) at much higher temperature is usually required if a precipitate must be converted to a more suitable form for weighing.



In this case, the weighed form of the precipitate might be different from the precipitated form.



# Examples:

## Some Commonly Employed Gravimetric Analyses

Substance Analyzed	Precipitate Formed	Precipitate Weighed
Fe	Fe(OH) <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
	Fe cupferrate	Fe <sub>2</sub> O <sub>3</sub>
Al	Al(OH) <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>
	Al(ox) <sub>3</sub> <sup>a</sup>	Al(ox) <sub>3</sub>
Ca	CaC <sub>2</sub> O <sub>4</sub>	CaCO <sub>3</sub> or CaO
Mg	MgNH <sub>4</sub> PO <sub>4</sub>	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>
Zn	ZnNH <sub>4</sub> PO <sub>4</sub>	Zn <sub>2</sub> P <sub>2</sub> O <sub>7</sub>
Ba	BaCrO <sub>4</sub>	BaCrO <sub>4</sub> same
SO <sub>4</sub> <sup>2-</sup>	BaSO <sub>4</sub>	BaSO <sub>4</sub> same
Cl <sup>-</sup>	AgCl	AgCl same
Ag	AgCl	AgCl same
PO <sub>4</sub> <sup>3-</sup>	MgNH <sub>4</sub> PO <sub>4</sub>	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>
Ni	Ni(dm <sub>g</sub> ) <sub>2</sub> <sup>b</sup>	Ni(dm <sub>g</sub> ) <sub>2</sub> same

<sup>a</sup>ox = Oxine (8-hydroxyquinoline) with 1 H<sup>+</sup> removed.

<sup>b</sup>dm<sub>g</sub> = Dimethylglyoxime with 1 H<sup>+</sup> removed.

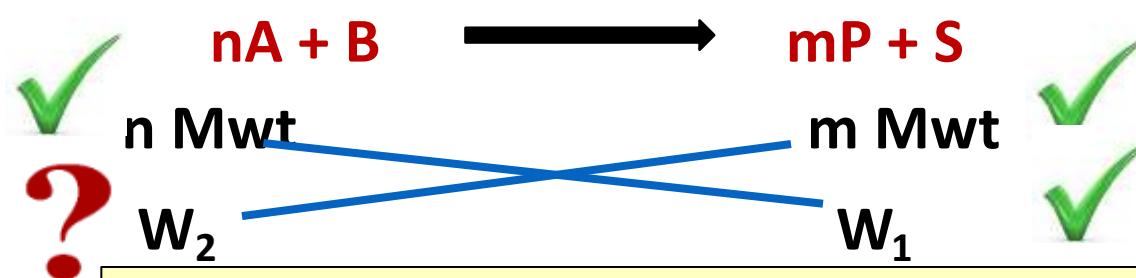
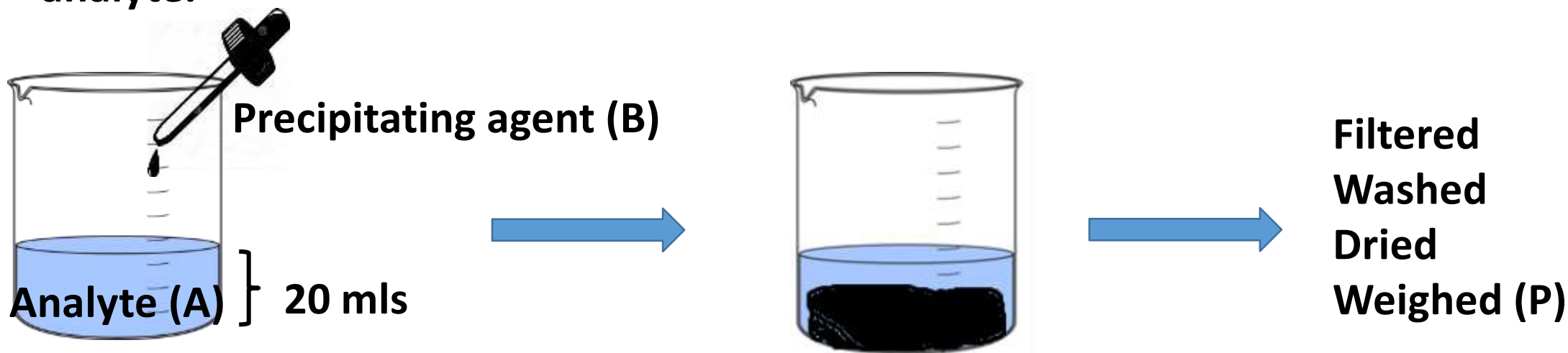


## 6- Weighing



# 7- Calculations

- Gravimetric calculations relate moles of the product finally weighed to moles of analyte.



Convert moles into weights by multiplying by the molecular weight.

• Where  $W_2$  is the weight of the **analyte ion** only dissolved in 20 ml of solution and  $W_1$  is the weight of **precipitate** (ppt).

$$\text{weight of the analyte } W_2 = \text{weight of the precipitate } W_1 \times \frac{n \text{ MW}_{\text{analyte}}}{m \text{ MW}_{\text{ppt}}}$$

$(n \text{ Mwt}_{\text{analyte}} / m \text{ Mwt}_{\text{ppt}})$  is called **the gravimetric factor**.



# Example 1

- Calculate the gravimetric factor for each of the following:



- $P/Ag_3PO_4 = \text{atwt } P / \text{Mwt } Ag_3PO_4$
- $K_2HPO_4/Ag_3PO_4 = \text{Mwt } K_2HPO_4 / \text{Mwt } Ag_3PO_4$
- $Bi_2S_3/BaSO_4 = \text{MWt } Bi_2S_3 / 3\text{MWt } BaSO_4$
- $As_2O_3/Ag_3AsO_4 = \text{Mwt } As_2O_3 / 2\text{MWt } Ag_3AsO_4$
- $K_2O/KB(C_6H_5)_4 = \text{Mwt } K_2O / 2\text{MWt } KB(C_6H_5)_4$

## Example 2

- Orthophosphate ( $\text{PO}_4^{3-}$ ) is determined by weighing as ammonium phosphomolybdate,  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ . Calculate the percent P in the sample and the percent  $\text{P}_2\text{O}_5$  if 1.1682 g precipitate were obtained from a 0.2711 g sample.
- Remember:  $\text{Wt of analyte} = \text{Wt of ppt} \times \text{Gravimetric Factor}$

$$\begin{aligned}\text{Wt of P} &= 1.1682 \times \frac{\text{At. wt P}}{\text{Mwt } (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3} = \\ &= 1.1682 \times \frac{30.97}{1876.5} = 0.0193 \text{ g}\end{aligned}$$

$$\% \text{ P} = (0.0193/0.2711) \times 100 = 7.11\%$$

## Example 2 (cont.)

**In general,**

$$\% \text{ppt} = \frac{\text{Wt}_{\text{ppt}} \times \text{gravimetric factor}}{\text{Wt of sample}} \times 100$$

$$\therefore \% \text{P}_2\text{O}_5 = \frac{1.1682 \times \frac{\text{Mwt P}_2\text{O}_5}{2 \text{ Mwt (NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3}}{0.2711} \times 100$$

$$= \frac{1.1682 \times \frac{141.95}{2 \times 1876.5}}{0.2711} \times 100 = 16.30\%$$

## Example 3

- An ore is analyzed for the manganese content by converting the manganese to  $\text{Mn}_3\text{O}_4$  and weighing it. If a 1.52 g sample yields  $\text{Mn}_3\text{O}_4$  weighing 0.126g, what would be the percent Mn and  $\text{Mn}_2\text{O}_3$  in the sample?

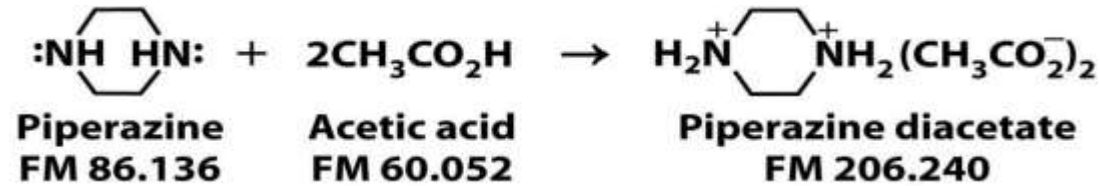
$$\begin{aligned}\% \text{Mn}_2\text{O}_3 &= \frac{0.126 \times \frac{3 \text{ Mwt Mn}_2\text{O}_3}{2 \text{ Mwt Mn}_3\text{O}_4}}{1.52} \times 100 \\ &= \frac{0.126 \times \frac{3 (157.9)}{2 (228.8)}}{1.52} \times 100 = 8.58\%\end{aligned}$$

## Example 3 (cont.)

$$\begin{aligned}\% \text{ Mn} &= \frac{0.126 \times \frac{3 \text{ At.wt Mn}}{\text{Mwt Mn}_3\text{O}_4}}{1.52} \times 100 \\ &= \frac{0.126 \times \frac{3 (54.94)}{228.8}}{1.52} \times 100 = 5.97\%\end{aligned}$$

## Example 4

The piperazine content of an impure commercial material can be determined by precipitating and weighing the diacetate



In one experiment, 0.3126 g of the sample was dissolved in 25 mL of acetone and 1 mL of acetic acid was added. After 5 min, the precipitate was filtered, washed with acetone, dried at 110 °C, and found to weigh 0.7121 g. What is the percent of piperazine in the commercial material?

$$\% \text{piperazine} = \frac{0.7121 \times \frac{\text{MW}_{\text{piperazine}}}{\text{MW}_{\text{ppt}}}}{0.3126} \times 100$$

$$= \frac{0.7121 \times \frac{86.136}{206.240}}{0.3126} \times 100 = 95.14\%$$

# References

- D. A. Skoog, D.A. West, F.J. Holler, S.R. Crouch, Analytical Chemistry, an introduction, 7th Edition, ISBN 0-03-020293-0 , (Chapter 8).
- Lecture 11 by [Dr. Nesrine El Gohary](#), GUC, SS 2016
- Lecture 10 by Prof. Rasha Elnashar, GUC, SS 2015.
- Lecture 8 by Dr. Raafat Faraghly, GUC, SS 2007