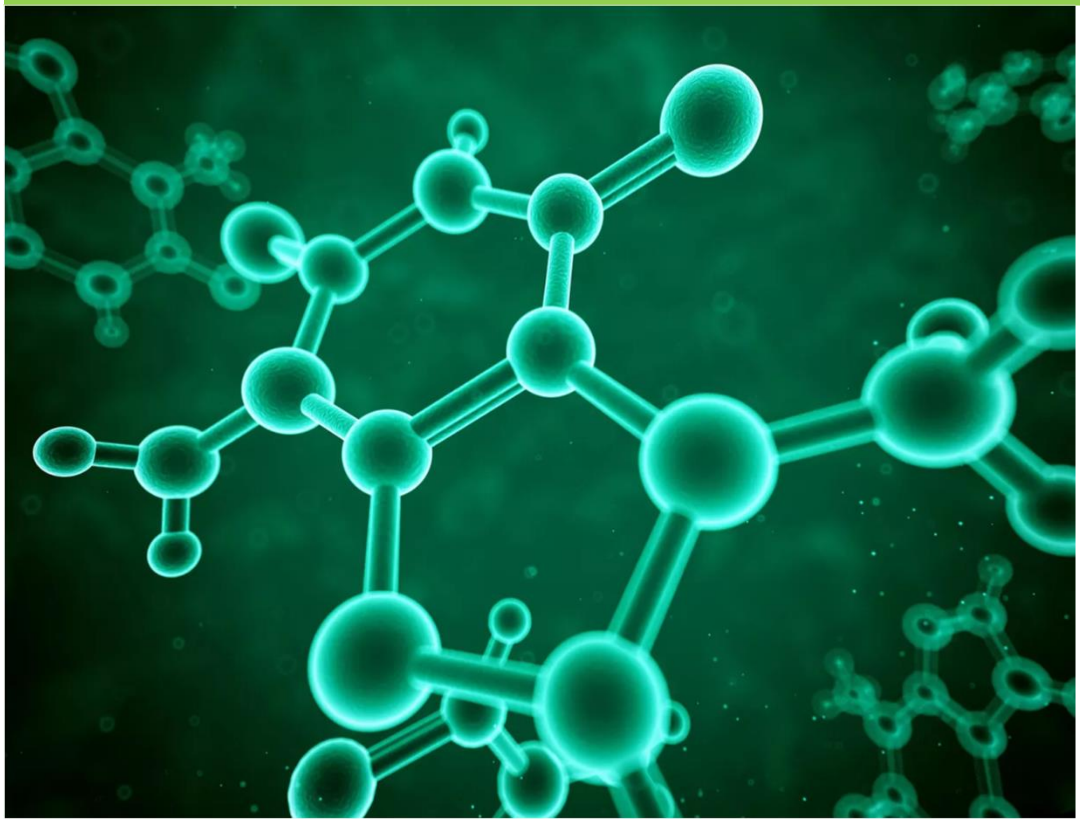
Analytical Chemistry



Dr. Ali Ehsan Hussein
University of Mosul /Faculty of Science
Forensic evidence department.

Lecture 4

❖ Precipitation gravimetry

- The analyte is converted to **a sparingly soluble precipitate** that is then **filtered**, **washed free of impurities** and converted to a **product of known composition** by **suitable heat** treatment and weighed.

Ex. for determining the [Ca2+] in water:

$$2NH_{3(aq)} + H_2C_2O_{4(aq)} \rightarrow 2NH_{4(aq)} + C_2O^{-2}{}_{4(aq)}$$

$$Ca^{+2}{}_{(aq)} + C_2O^{-2}{}_{4(aq)} \rightarrow CaC_2O_{4(s)}$$

Filtered , dried , ignited

$$CaC2O4(s) + \Delta \rightarrow CaO_{(s)} + Co_{(g)} + CO_{2(g)}$$

After cooling , the precipitate is weighed and the mass is determined.

❖ Particle size and filterality of precipitates

➢ Characteristics of Ion, colloid and particle

- ✓ The particle size of solids formed by precipitation varies enormously. At one extreme are **colloidal suspensions**, whose tiny particles are invisible to the naked eye (**10^{-7} to 10^{-4} cm in diameter**). Colloidal particles show no tendency to settle from solution and are difficult to filter.
- ✓ At the other extreme are particles with dimensions on the order of tenths of a millimeter or greater. The temporary dispersion of such particles in the liquid phase is called a **crystalline suspension**. The particles of a crystalline suspension tend to settle spontaneously and are easily filtered.

Name	Diameter	Characteristics
Ion	10^{-8} cm	Dissolved
Colloidal	10^{-7} to 10^{-4} cm	suspended
Crystalline	$>10^{-4}$ cm	Settled from solution (filterable)

- **precipitates consisting of large particles are generally desirable for gravimetric work because :**

1. These particles are easy to filter and wash free of impurities
2. precipitates of these type are usually purer than are precipitates made up fine particles.

- **The particles size of solids formed by precipitation varies enormously .therefore two type of precipitate occur as follows**

1. Colloidal suspension :

- Tiny particles are invisible to the naked eye (10^{-7} - 10^{-4} cm in diameter)
- its shows no tendency to settle from solution and are not easy filtered.
- its very difficult to filter the particles of a Colloidal suspension to trap these particles.

- The pore size of the filtering medium must be so small that filtration take a very long time with suitable treatment ,however the indivitual colloidal particles can be made to **stick together** or **coagulate** to produce large particles that are easy to filter.

2. **Crystal suspensions. > 10 $^{-4}$**

- its temporary dispersion of such particles in the liquid phase.
- the particles of crystalline suspension tend to **settle spontaneously** and are **easy filtered**.

❖ The experimental variables that effect on the particle size of precipitate are summarized as :

1. Precipitate solubility
2. Temperature
3. Concentration of reactant.
4. The rate at which reactant are mixed.

- The net effect of these variables can be accounted for at least qualitatively by assuming that the particle size is related to a single property of the system called relative supersaturation .

Relative supersaturation (Rss) :

Size of particles influenced by the relative supersaturation of the solutions in which is formed :

Relative supersaturation (Rss) = (Q – S) / S

Q: the concentration of the solute at any instant

S : the concentration solute at equilibrium

- **supersaturation :**

solution that contains a higher solute concentration than a saturated solution.

- Generally, precipitation reactions are slow so that, even when a precipitating reagent is added drop by drop to a solution of an analyte, some supersaturation is likely.
- Experimental evidence indicates that the particle size of a precipitate varies inversely with the average relative supersaturation during the time when the reagent is being introduced.
- Thus, when **(Q - S)/S is large**, the precipitate tends to be colloidal, and when **(Q - S)/S is small**, a crystalline solid is more likely.

RSS	Result
Large	Smaller particles (colloidal)
Small	Larger Particle (Crystalline)

❖ Experimental Control of Particle Size

✓ usually keeping Q is low(decrease) and S is high(increase) during precipitation.

Several steps are commonly taken to maintain favorable condition for the precipitation process.

$$RSS = \frac{Q - S}{S}$$

We can keep RSS small ((the lower RSS value the larger particles) by :

❑ **Increase S:**

✓ Heating to increase solubility.(hot solution)

✓ pH adjustment (If the solubility of the precipitate depends on pH).

✓ Adding complexing agent.

❑ **Decrease Q:**

✓ Using dilute precipitating solution

✓ Adding precipitating agent slowly and stirring.

✓ Using homogeneous precipitation technique.

❖ Colloidal suspension

- ✓ Daimeter = 10^{-7} to 10^{-4} cm
- ✓ Invisible to naked eye
- ✓ Not easy filtered , don't settle out of solution

❖ Crystalline suspension

- ✓ Diameter > 10^{-4}
- ✓ Spontaneously settle out of solution
- ✓ Readily filtered and washed free of impurities

Name	Diameter	Characteristics
Ion	10^{-8} cm	Dissolved
Colloidal	10^{-7} to 10^{-4} cm	suspended
Crystalline	**>10^{-4} cm**	**Settled from solution (filterable)**

Washing

- Washing of the sample in gravimetric analysis refers to the process of removing impurities.
- excess reagents, or soluble substances from the precipitate after it has been separated from the solution through filtration.
- This step is essential to ensure that the precipitate is pure and only contains the analyte of interest, leading to more accurate and reliable results.
- Distilled water is commonly solvent used for washing the precipitate in gravimetric analysis.
- Distilled water is neutral and does not contain ions that could contaminate the precipitate

- the precipitate separated from its solution remains on the filter paper to remove the impurities on the precipitate, it needs to be washed with a suitable solvent(<u>Distilled water).</u>

- <u>The solvent used for washing needs to have some properties :</u>

1. It shouldn't affect the solubility of the precipitate , it should only help to dissolve impurities
2. it shouldn't form a volatile compound with the precipitate.
3. it should be volatile to be removed with impurities from the precipitate easy.

❖ Calculation of result from gravimetric data

✓ Gravimetric factor(Gf):

The ratio of **molar mass of the sought substance** to molar mass of **gravimetric formula** is called as Gravimetric factor, Gf But in both formulas, atoms or molecules need to be found for same number of components.

$$G_f = \frac{a}{b} \times \frac{M_{\text{sought substance}}\,(g/mol)}{M_{\text{Mass formula}}\,(g/mol)}$$

In this formula, a and b shows the lowest numbers for two compounds to have the same sought substance (analyet) in numerator and denominator. Below are examples on how gravimetric factor is calculated.

Example

Calculate the gravimetric factor of chloride (sought substance) in AgCl (mass formula) precipitate. (M_{AgCl}= 143.5 g/mol), (M_{Cl}= 35.5 g/mol) Solution:

In this example, chloride is the sought substance. AgCl is accepted as gravimetric formula.

$$G_f = \frac{a}{b} \times \frac{M_{Cl}\ (g/mol)}{M_{AgCl}\ (g/mol)}$$

As both formulas contain the same number of chloride atoms, a and b are both equal to 1. Therefore, **Gf** which is gravimetric factor of silver chloride is calculated as follows:

$$G_f = \frac{1}{1} \times \frac{35.5\ (g/mol)}{143.5\ (g/mol)} = 0.25$$