Republic of Iraq
Ministry of Higher Education & Scientific research
Al-Mustaqbal University
Science College
Medical physics Department

Analytical Chemistry

For

First Year Student

Lecture 5

By

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Gravimetric Methods of analysis

Gravimetric methods: are quantitative methods that are based on determining the mass of a pure compound to which the analyte is chemically related.

Types of Gravimetric Analysis

1- **Precipitation gravimetry**: The analyte is separated from a solution of the sample as a precipitate and is converted to a compound of known composition that can be weighed.

2- Volatilization gravimetry: The analyte is separated from other constituents of a sample by converting it to a gas of known chemical composition that can be weighed.

3- Electrogravimetry: The analyte is separated by deposition on an electrode by an electrical current.

Advantages of gravimetric analysis:

1- Tradition method.

2- Cheap, easily available apparatus, simple to carry out.

3- Slow, especially when accurate results are required.

4- Wide range of concentration (ng-kg).

5- No calibration required except for the balance.

6- Accurate.

Disadvantages of gravimetric analysis:

i. Proper lab technique is critical

ii. Careful and time consuming.
iii. Very clean glassware.
iv. Very accurate weighing.
v. Co-precipitation.

Example for Precipitation: determining the [Ca$^{2+]}$ in water:

$2NH_3 + H_2C_2O_4 \rightarrow 2NH4+ + C_2O_4^{-2}$

$Ca^{+2} (aq) + C_2O_4^{-2} (aq) \rightarrow CaC_2O_4 (s)$

filtered, dried, ignited

$CaC_2O_4 + \Delta \rightarrow CaO (s) + CO (g) + CO_2$

The step required in gravimetric analysis:

- Preparation the solution
- Precipitation
- Digestion
- Filtration
- Washing
- Drying and igniting
- Weighing
- Calculation

1. Properties of Precipitates and Precipitating Reagents

A gravimetric precipitating agent should react specifically or at least selectively with the analyte and give precipitates that is:

1. Enough particle size for retaining on filter paper

2. High purity (free of contaminants)

3. Low solubility that no significant loss of the analyte occurs during filtration and washing

4. Unreactive with air (stable)

5. Known stoichimetric composition after it is dried or, if necessary, ignited

* Specific reagents: react only with a single chemical species.

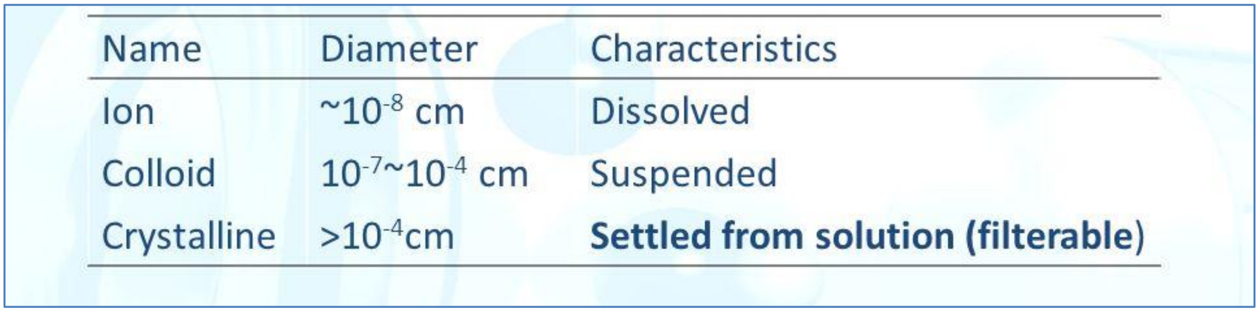
* Selective reagents: react with a limited number of species.

2. Particle Size and Filterability 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
Colloid	10^{-7}~10^{-4} cm	Suspended
Crystalline	>10^{-4}cm	**Settled from solution (filterable)**

Precipitates consisting of large particles are generally desirable for gravimetric work because these particles are easy to filter and wash free of impurities.

Factors That Determine the Particle Size of Precipitates

Precipitate formation has been studied for many years, but the mechanism of the process is still not fully understood. What is certain, however, is that the particle size of a precipitate is influenced by

* precipitate solubility.

* temperature.

* reactant concentrations.

* rate at which reactants 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**, where:

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

Q: the concentration of the solute at any instant.

S: the concentration solute at equilibrium.

Relative supersaturation (RSS)

A supersaturated solution is an unstable solution that contains a higher solute concentration than a saturated solution. As excess solute precipitates with time, supersaturation decreases to zero.

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	Process	Result
Large	Nucleation dominate	Smaller particles (colloidal)
Small	Particle growth dominate	Larger Particle (Crystalline)

Mechanism of Precipitate Formation

Nucleation and Particle growth

- Nucleation: The initial formation process in which a minimum number of atoms, ions, or molecules join together to give a stable solid.

- Often, these nuclei form on the surface of suspended solid contaminants, such as dust particles

- Particle growth: The subsequent growth after nucleation.
  - If nucleation predominates, a precipitate containing a large number of small particles results.
  - if growth predominates, a smaller number of larger particles is produced.

RSS	Process	Result
Large	Nucleation dominate	Smaller particles (colloidal)
Small	Particle growth dominate	Larger Particle (Crystalline)

Experimental Control of Particle Size

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

(the lower RSS value the larger particles)

Increase S:

- Heating to increase solubility
- 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.

3. Colloidal Precipitates

Individual colloidal particles are so small that they are not retained by ordinary filters. Moreover, Brownian motion prevents their settling out of solution under the influence of gravity.

Fortunately, however, we can coagulate, or agglomerate, the individual particles of most colloids to give a filterable, amorphous mass that will settle out of solution. (**When liquid starts to thicken and become solid, it coagulates**)

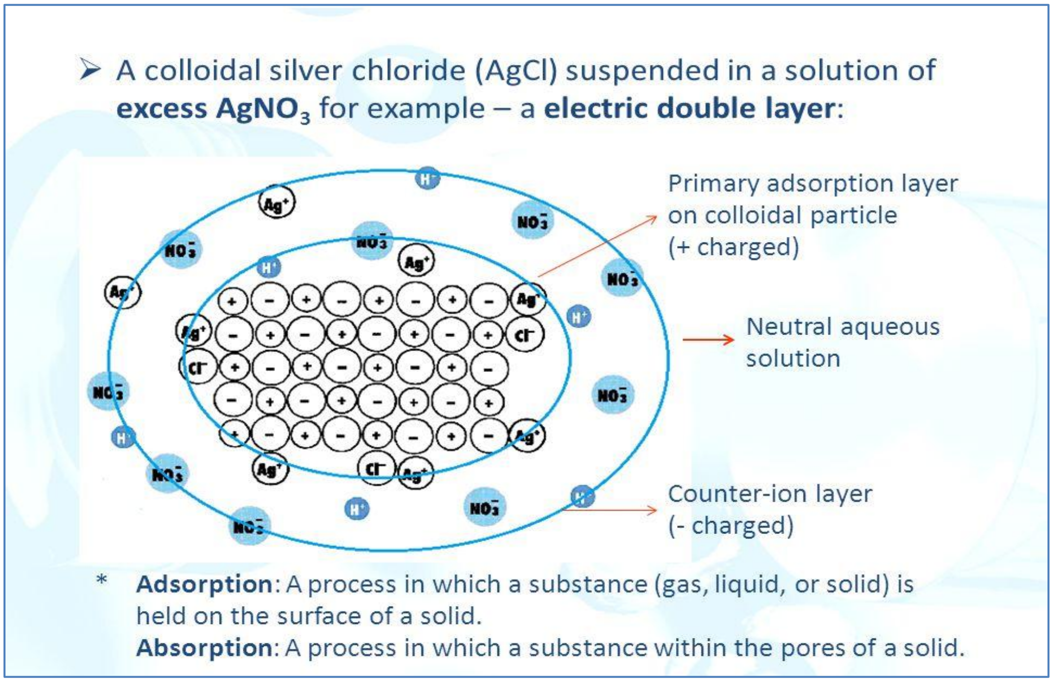
(agglomeration: a large group of many different things collected or brought together)

Coagulation of Colloids:

Coagulation can be hastened by heating, by stirring, and by adding an electrolyte to the medium.

why colloidal suspensions are stable and do not coagulate spontaneously?

Colloidal suspensions are stable because all of the particles of the colloid are either positively or negatively charged and thus repel one another. The charge results from cations or anions that are bound to the surface of the particles.



- A colloidal silver chloride (AgCl) suspended in a solution of **excess $AgNO_3$** for example – a **electric double layer**:

Primary adsorption layer on colloidal particle (+ charged)

Neutral aqueous solution

Counter-ion layer (- charged)

* **Adsorption**: A process in which a substance (gas, liquid, or solid) is held on the surface of a solid.
Absorption: A process in which a substance within the pores of a solid.

4.**Coprecipitation**

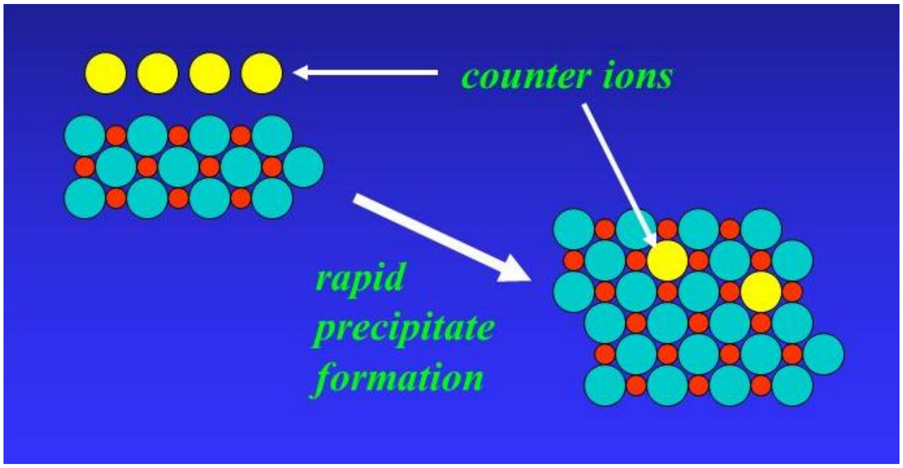
A process in which normally soluble compounds are carried out of solution by a precipitate. It may resulted in impurities within the desired precipitates. Coprecipitated impurities may cause either negative or positive errors.

There are four types of coprecipitation:

- ✓ surface adsorption
- ✓ mixed-crystal formation
- ✓ occlusion
- ✓ mechanical entrapment.
  - ✓ **Occlusion**

A type of co-precipitation in which a compound (foreign ions in the counter-ion layer) is physically trapped within a precipitate during rapid precipitate formation.

- o Problem solving: Digestion



Digestion: The process which has a waiting time to achieve desired outcome. (The solubility–precipitation is in a dynamic equilibrium, digestion ensures the occluded material is eventually exposed to the supernatant solution.)

5. **Drying and Ignition of Precipitates**

A gravimetric precipitate is heated until its mass becomes constant.

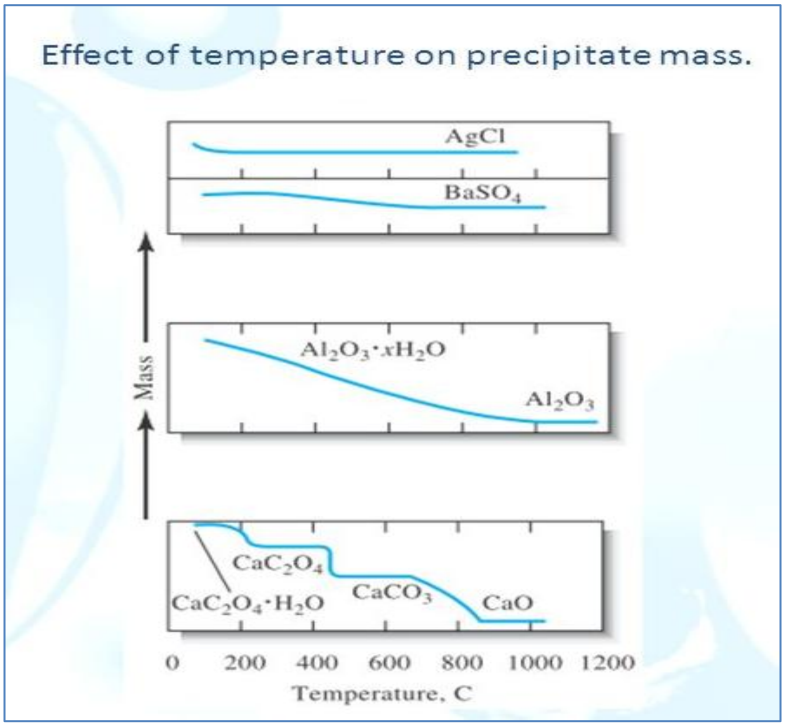
- Heating removes the solvent and any volatile species carried down with the ppt.
- Some precipitates are also ignited to decompose the solid and form a compound of known composition. This new compound is often called the weighing form.

i. The temperature required to dehydrate a precipitate completely may be as low as 100°C or as high as 1000°C

ii. Moisture is completely removed from silver chloride at temperatures higher than 110°C, but dehydration of aluminum oxide is not complete until a temperature greater than 1000°C is achieved.

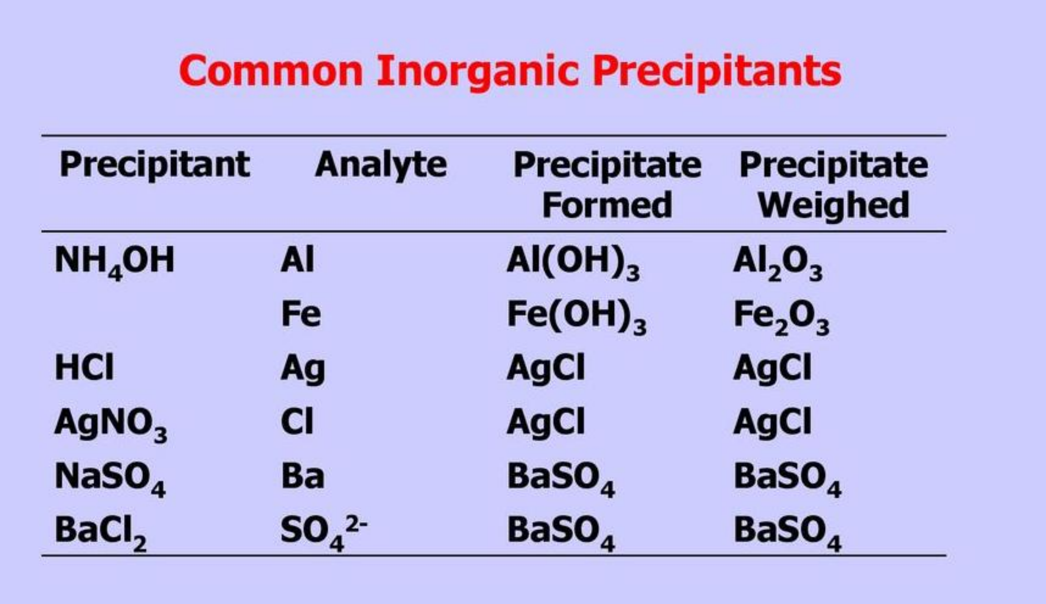
iii. The thermal curve for calcium oxalate is considerably more complex than the others

iv. Recording thermal decomposition curves is called thermogravimetric analysis, and the mass versus temperature curves are termed thermograms.


Effect of temperature on precipitate mass.

Applications of gravimetric methods

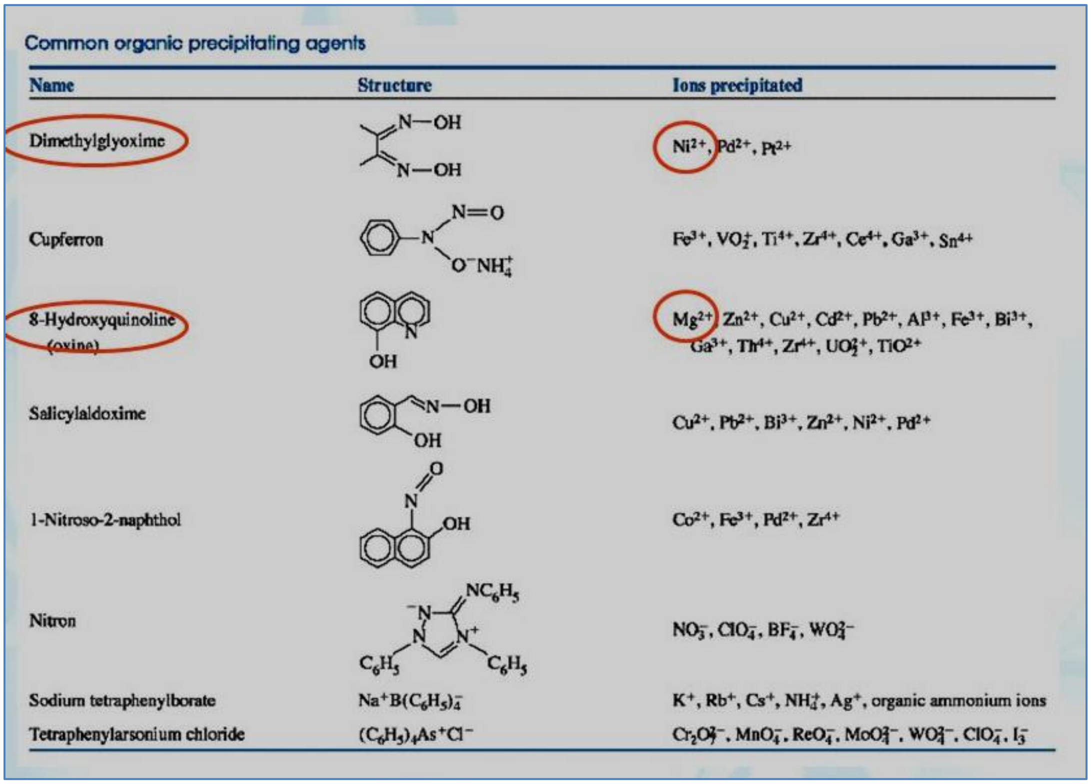
1- Inorganic Precipitating Agents



Common Inorganic Precipitants

Precipitant	Analyte	Precipitate Formed	Precipitate Weighed
NH_4OH	Al	$Al(OH)_3$	Al_2O_3
	Fe	$Fe(OH)_3$	Fe_2O_3
HCl	Ag	AgCl	AgCl
$AgNO_3$	Cl	AgCl	AgCl
$NaSO_4$	Ba	$BaSO_4$	$BaSO_4$
$BaCl_2$	SO_4^{2-}	$BaSO_4$	$BaSO_4$

2-Organic Precipitating Agents



Common organic precipitating agents

Name	Structure	Ions precipitated
Dimethylglyoxime		Ni^{2+}, Pd^{2+}, Pt^{2+}
Cupferron		Fe^{3+}, VO_2^+, Ti^{4+}, Zr^{4+}, Ce^{4+}, Ga^{3+}, Sn^{4+}
8-Hydroxyquinoline (oxine)		Mg^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Fe^{3+}, Bi^{3+}, Ga^{3+}, Th^{4+}, Zr^{4+}, UO_2^{2+}, TiO^{2+}
Salicylaldoxime		Cu^{2+}, Pb^{2+}, Bi^{3+}, Zn^{2+}, Ni^{2+}, Pd^{2+}
1-Nitroso-2-naphthol		Co^{2+}, Fe^{3+}, Pd^{2+}, Zr^{4+}
Nitron		NO_3^-, ClO_4^-, BF_4^-, WO_4^{2-}
Sodium tetraphenylborate	$Na^+B(C_6H_5)_4^-$	K^+, Rb^+, Cs^+, NH_4^+, Ag^+, organic ammonium ions
Tetraphenylarsonium chloride	$(C_6H_5)_4As^+Cl^-$	$Cr_2O_7^{2-}$, MnO_4^-, ReO_4^-, MoO_4^{2-}, WO_4^{2-}, ClO_4^-, I_3^-