Particle Size and Filterability of Precipitate:

Characteristics of Ions, colloids and particles

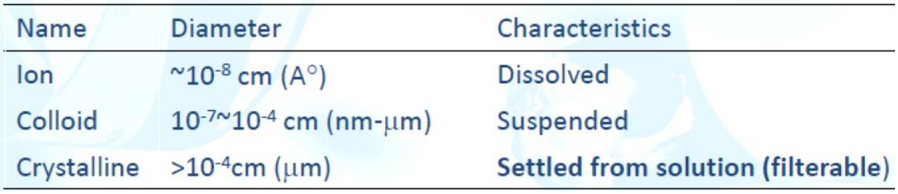
The particle size of solids formed by precipitation varies enormously.

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.**

Precipitates consisting of large particles are generally desirable for gravimetric work because

1. large particles are easy to filter and wash.
2. they are less soluble.
3. they are usually purer



Name	Diameter	Characteristics
Ion	~10^{-8} cm (A°)	Dissolved
Colloid	10^{-7}~10^{-4} cm (nm-μm)	Suspended
Crystalline	>10^{-4}cm (μm)	**Settled from solution (filterable)**

Precipitates are formed in two steps

1- Nucleation: This step includes the formation of small particles called nuclei. These nuclei do not appear directly after the addition of precipitating agent, there is a time period between the mixing of reactants and visual appearing of the precipitate, this period is called "induction period". This period varies according to the type of the precipitate.

2- Particle growth: Involves coagulation of these nuclei to form larger particle size precipitate.

When a precipitate is formed at high relative supersaturation, nucleation is the major precipitation mechanism:

A large number of small particles will be formed Colloidal precipitate

When a precipitate is formed at low relative supersaturation the rate of particle growth predominates

A Large particle size formed Crystalline precipitate results

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:

1- Precipitate solubility
2- Temperature

3. Reactant concentrations
4. The rate at which reactants are mixed

The effects 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 (RSS)**, and that can presented by Von Weimarn equation

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

Q = The concentration of the solute at any instant

S= The concentration solute at equilibrium (Solubility)

A large, positive value of *RSS* indicates that a solution is highly supersaturated. Such solutions are unstable and show high rates of nucleation, producing a precipitate consisting of numerous small particles. When *RSS* is small, precipitation is more likely to occur by particle growth than by nucleation.

Examining Von-Weimarn equation shows that we can minimize *RSS* by either decreasing the solute's concentration or increasing the precipitate's solubility. A precipitate's solubility usually increases at higher temperatures, and adjusting pH may affect a precipitate's solubility if it contains an acidic or basic anion. Temperature and pH, therefore, are useful ways to increase the value of *S.* Conducting the precipitation in a dilute solution of analyte, or adding the precipitant slowly and with vigorous stirring are ways to decrease the value of *Q*.

$$RSS\ \alpha\ \frac{1}{particale\ size}$$

Thus when Q-S/S is large Colloidal precipitates will be formed

When Q-S/S is small Crystalline precipitates will be formed.

thus we can control the particle size experimentally by

Increase S:

1. Heating to increase solubility
2. pH adjustment (If the solubility of the precipitate depends on pH)
3. Adding complexing agent

***Decrease Q*:**

1. Using dilute precipitating solution
2. Adding precipitating agent slowly and stirring
3. Using homogeneous precipitation technique
4. Precipitation from Homogeneous Solution

Types of precipitating agents:

1- Inorganic precipitating agents:

These reagents from slightly soluble salts or hydrous oxides with the analyte. Most inorganic reagents are not very selective

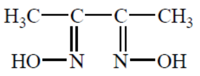
Some inorganic precipitating agents:

Precipitating agent	Element precipitated
NH_3 (aq.)	Be(BeO), Al(Al_2O_3), Se(Se_2O_3), Cr(Cr_2O_3), Fe(Fe_2O_3), Ga(Ga_2O_3), Zr(ZrO_2)
H_2S	Cu(CuO), Zn(ZnO or $ZnSO_4$), Ge(GeO_2), As(As_2O_3 or As_2O_5), Bi(Bi_2S_3)……
$(NH_4)_2S$	Hg(HgS), Co(Co_3O_4)
H_2SO_4	Li, Mn, Sr, Cd, Pb, Be, (all as sulphate)
H_2PtCl_6	K(K_2PtCl_6), Rb($RbPtCl_6$), Cs($CsPtCl_6$)
$H_2C_2O_4$	Ca(CaO), Sr(SrO), Th(ThO_2)
HCl	Ag(AgCl), Hg(Hg_2Cl_2)
$AgNO_3$	Cl(AgCl), Br(AgBr), I(AgI)
$(NH_4)_2CO_3$	Bi(Bi_2O_3)
NH_4SCN	Cu[$Cu_2(SCN)_2$]
HNO_3	Sn(SnO_2)
$BaCl_2$	SO_4^{-2}($BaSO_4$)
$MgCl_2.NH_4Cl$	PO_4^{-2}($Mg_2P_2O_7$)

2- Organic precipitating agents:

Numerous organic reagents have been developed for the gravimetric determination of inorganic species, some of these reagents are **more selective** in their reactions than most of the inorganic reagents. There are two types of organic reagents:

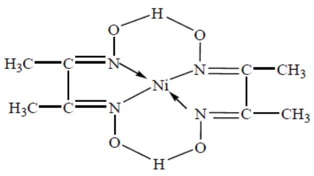
A- Complex forming agents: these substances capable of forming insoluble compounds with ions, usually with metal ions. They have an acid group at one point on the molecule, a basic atom or group at another point, and sufficient atoms between the two points to produce a ring of five or six members after bonding with metal atom. The resulting compound is called a chelate compound for example **Dimethylglyoxime** It is a quite specific reagent for precipitating Ni(II) and Pd(II). The Ni(II) compound precipitates in slightly basic (alkaline) solution while Pd(II) compound can be precipitated from acid solutions



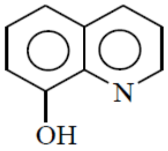
$$H_3C-\underset{\underset{HO-N}{\|}}{C}-\underset{\underset{N-OH}{\|}}{C}-CH_3$$

Dimethylglyoxime

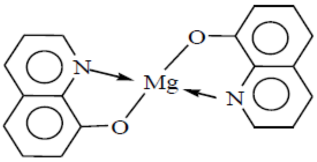
The formula of nickel dimethylglyoxime is :



Another example is 8-hydroxyquinoline that also called oxine, The formula of chelate compound is forms with magnesium can be represented as follows:



8-Hydroxyquinoline



Oxine reacts with many metal ions (~ 24) according to the pH of the solution

Ca^{+2}, Mg^{+2} pH ~8

Al^{+3} pH ~4

Th^{+4}, Zr^{+4} pH ~3

The pH of reaction of oxine with metal ions decrease with increasing the oxidation state of the metal ion.

B-Salt forming agents:These are substances which form non-ionic crystalline insoluble precipitates for example sodium tetraphenylboron $NaB(C_6H_5)_4$ it is useful for precipitating potassium or ammonium as $KB(C_6H_5)_4$ or $NH_4B(C_6H_5)_4$ tetraphenylarsonium chloride $[(C_6H_5)_4As]Cl$ it is useful in precipitating negative ions

$$(C_6H_5)_4As^+Cl^- \longrightarrow (C_6H_5)_4As^+ + Cl^-$$

$$(C_6H_5)_4As^+ + X^{-n} \longrightarrow [(C_6H_5)_4As]_nX \downarrow$$

$$X^{-n} = MnO_4^-,\ Cr_2O_7^{-2},\ WO_4^-,\ MoO_4^{-2},\ SnCl_6^{-2}$$

Benzidine is other example that used for sulphate ions (SO_4^{-2}) and phosphate ions (PO_4^{-3}) precipitation.

Advantages of methods of precipitation with organic reagents:

1- Organic reagents are either selective or can be made to be selective by masking or by pH adjustment of the solution.
2- The precipitates are usually not ionic and do not adsorb impurities strongly.
3- The precipitates are easily dried at temperatures slightly above 100oC.
4- Small amount of the precipitating ion yields relatively large amount of a precipitate. This reduces relative errors which result during drying, transferring and weighing.
5- The precipitates are generally soluble in organic solvents, therefore, they can be **separated by extraction** with a solvent as well as by precipitation. If the solution is coloured, the amount of the analyte can be quickly determined by spectrophotometric methods.

Disadvantages of organic precipitating reagents:

1. Precipitates are almost always sticky. They adhere strongly to glassware and are difficult to transfere from vessel to vessel. The use of polyethylene ware sometimes reduces this problem.
2. **Organic reagents are generally not pure** as the synthesis of most organic reagents is not perfect and purification is often incomplete.
3. **Organic precipitating agents are only slightly soluble in the precipitation solution**. A small excess of reagent may result in contamination of the precipitate by the reagent itself.