College of science for women
Department of Chemistry

Second Stage

Gravimetric Analysis

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- **Steps Involved in Gravimetric Analysis**
- 1. Preparation of the solution
- 2. Precipitation
- 3. Digestion
- 4. Filtration
- 5. Washing of the Precipitate
- 6. Drying or igniting
- 7. Weighing

8. Calculation •

1.**Preparation of the Solution**

This may involve several steps including adjustment of the pH of the solution in order for the precipitate to occur quantitatively and get a precipitate of desired properties, removing interferences …etc.

- **2.Precipitation**
- This requires addition of a precipitating agent solution to the sample solution. Upon addition of the first drops of the precipitating agent, supersaturation occurs, then nucleation starts to occur where every few molecules of precipitate aggregate together forming a nucleus. At this point, addition of extra precipitating agent will either form new nuclei (precipitate with small particles) or will build up on existing nuclei to give a precipitate with large particles .

3.. This can be predicted by Von Weimarn ratio where, according to this relation the particle size is inversely proportional to a quantity called the relative supersaturation where Relative Supersaturation = $(Q – S) / S$ The Q is the concentration of reactants before precipitation at any point , S is the solubility of precipitate in the medium from which it is being precipitated. Therefore, in order to get particle growth instead of further nucleation (i.e granular precipitate and then low surface area) we need to make the relative supersaturation ratio as small as possible. In other words conditions need to be adjusted such that Q will be as low as possible and S will be relatively large

- The optimum conditions for precipitation which make the supersaturation low are:

- a.Precipitation using dilute solutions to decrease Q
- b.Slow addition of precipitating agent to keep Q as low as possible
- c.Stirring the solution during addition of precipitating agent to avoid concentration sites and keep Q low .
- d.Increase solubility S by precipitation from hot solution .
- e.Adjust the pH in order to increase S but not too much increase as we do not want to loose precipitate by dissolution .
- f.Precipitation from Homogeneous Solution: In order to make Q minimum we can, in some situations, generate the precipitating agent in the precipitation medium rather than adding it. For example, in order to precipitate iron as the hydroxide, we dissolve urea in the sample. Heating of the solution generates hydroxide ions from the hydrolysis of urea. Hydroxide ions are generated at all points in solution and thus there are no sites of concentration. We can also adjust the rate of urea hydrolysis and thus control the hydroxide generation rate. This type of procedure can be very advantageous in case of colloidal precipitates.
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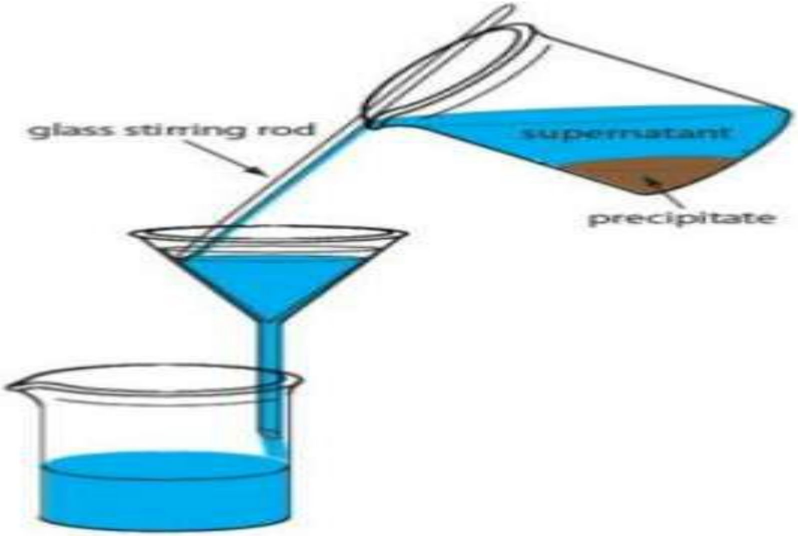
- **3- Digestion of the Precipitate**:

- The precipitate is left hot (below boiling) for 30 min to 1 hour in order for the particles to be digested. Digestion involves dissolution of small particles and reprecipitation on larger ones resulting in particle growth and better precipitate characteristics. This process is called Ostwald ripening. An important advantage of digestion is observed for colloidal precipitates where large amounts of adsorbed ions cover the huge area of the precipitate. Digestion forces the small colloidal particles to agglomerate which decreases their surface area and thus adsorption.
- The precipitate often contains ions that where trapped when the precipitate was formed. This is mostly a problem for crystalline precipitates. If the trapped ions are not volatile, then their presence will corrupt the weighing step. Concentration of interfering species may be reduced by digestion. Unfortunately , postprecipitation as we will see later will increase during digestion .

- **4-Washing and Filtering**
- Problems with surface adsorption may be reduced by careful washing of the precipitate. With some precipitates, peptization occurs during washing. Each particle of the precipitate has two layers , in primary layer certain ions are adsorbed and in the outer layer other ions of opposite charge are adsorbed . This situation makes the precipitate settle down . If the outer layer ions are removed then all the particles will have the same charge so the particles will be dissonant . This is called peptization
- This results in the loss of part of the precipitate because the colloidal form may pass through on filtration. , in case of colloidal precipitates we should not use water as a washing solution since peptization would occur. In such situations dilute volatile electrolyte such as nitric acid, ammonium nitrate, or dilute acetic acid may be used.

- Usually, it is a good practice to check for the presence of precipitating agent in the filtrate of the final washing solution. The presence of precipitating agent means that extra washing is required. Filtration should be done in appropriate sized Goosh or ignition ashless filter paper. After the solution has been filtered, it should be tested to make sure that the analyte has been completely precipitated. This is easily done by adding a few drops of the precipitating reagent to the filtrate ; if a precipitate is observed, the precipitation is incomplete. The common ion effect can be used to reduce the solubility of the precipitate. When Ag^+ is precipitated out by addition of Cl^- $Ag^+ + Cl^- \rightarrow AgCl\,(s)$ The (low) solubility of AgCl is reduced still further by the excess of Ag^+ which is added, pushing the equilibrium to the right . It important to know that the excess of the precipitating agent should not exceed 50%

- of its equivalent amount , otherwise the precipitating agent may form a soluble complex with the precipitate : $AgCl + Cl^-$ → $AgCl_2^-$ (soluble complex) The following graph shows that most precipitates follow this pattern, but there are some anomalies such as Hg_2I and $BaSO_4$.



- **5- Drying and Ignition**
- The purpose of drying (heating at about 120-150 oC in an oven) is to remove the remaining moisture while the purpose of ignition in a muffle furnace at temperatures ranging from 600-1200 oC is to get a material with exactly known chemical structure so that the amount of analyte can be accurately determined . The precipitate is converted to a more chemically stable form. For instance, calcium ion might be precipitated using oxalate ion, to produce calcium oxalate (CaC_2O_4) which is hydrophil , therefore it is better to be heated to convert it into $CaCO_3$ or CaO . The $CaCO_3$ formula is preferred to reduce weighing errors as mentioned in previous lectures .
- It is vital that the empirical formula of the weighed precipitate be known, and that the precipitate be pure; if two forms are present, the results will be inaccurate.

Ashless filter paper

Porcelain crucible

(Ignition up to 1000 □C)

Glass crucible

(Drying at 100-120 □C)

- **6-Weighing the precipitate**
- The precipitate can not be weighed with the necessary accuracy in place on the filter paper; nor can the precipitate be completely removed from the filter paper in order to weigh it.
- The precipitate can be carefully heated in a crucible until the filter paper has burned away; this leaves only the precipitate. (As the name suggests, "ashless" paper is used so that the precipitate is not contaminated with ash.) . If you use Goosh crucible then after the precipitate is allowed to cool (preferably in a desicator to keep it from absorbing moisture), it is weighed (in the crucible). The mass of the crucible is subtracted from the combined mass, giving the mass of the precipitated analyte. Since the composition of the precipitate is known, it is simple to calculate the mass of analyte in the original sample.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