2. Precipitation methods

Many metallic elements in their ionic forms react with negative counter ions to produce stable precipitates. Silver ions form stable and highly insoluble salts with chloride, bromide and iodide. Calcium precipitates quantitatively with oxalate and can be measured reproducibly at any of three temperature dependent plateaus as the oxalate, the carbonate and the oxide. Barium precipitates quantitatively as the sulfate. The reactions often follow the same patterns.

$$Ag^{+} + Cl^{-} \rightarrow AgCl \downarrow$$

$$Ca^{+2} + C_2O_4^{-2} \rightarrow CaC_2O_4 \overset{\emptyset}{\rightarrow} CaCO_3 \; or \; CaO \;\; depend\ on\ the\ temp.$$

$$Ba^{+} + SO_4^{-2} \rightarrow BaSO_4 \downarrow$$

In **Precipitation methods** the analyte (the component to be determined) which is soluble in aqueous solution is converted into a sparingly soluble material called "precipitate" after the addition of a certain chemical reagent called precipitating agent.

A precipitation gravimetric analysis must have several important attributes. First, the precipitate must be of ***low solubility***, ***high purity***, and of ***known composition*** if its mass is to accurately reflect the analyte's mass. Second, the precipitate must be in a form that is ***easy to separate from the reaction mixture***.

Steps of the gravimetric methods of analysis:

1. ***Sampling (treatment of the sample):***
   For solid samples: the sample must be *grinding* to the smaller size particles to obtain the most homogeneous form and one gram of the sample is taken this must contains all the original sample constituents .
   Liquid and gaseous samples are simply converted to a homogenous form.

   The second step of sampling is *the drying of the samples*:
   Most samples originally consist some moisture so the sample must be dried to a certain temperature enough for evaporation of water molecules. After the drying step the sample must be kept in the absence of moisture. The other step of sampling is weighing of the sample using sensitive balances (weighing of liquid samples are more complicated than solid ones).
2. ***Dissolution of the sample:***
   Choosing the right solvent to dissolve a sample is strongly depends on the nature of that sample continues, for example, distilled water, acids or bases are used to dissolve **inorganic samples** and form a homogeneous solution. Thus, we usually use this sequence to test the solubility of inorganic samples.
   a. **Distilled water**: first we usually start to use **cold distilled water** to dissolve samples but if we face any difficulties in this process such as forming inhomogeneous solutions or leaving some non-soluble particles in the solution, we have to heating the solution **"using hot distilled water"** to increase the solid solubility and thus, form

homogeneous solutions. For example, KCl, NaCl, KNO_3 and $NaNO_3$ easily dissolved in cold water while their sulfate salts such Na_2SO_4 need to use hot distilled water to dissolve it.

b. **Strong and Weak acids**: $HClO_4$, HCl, HNO_3 are strong acids more which usually favorite than weak acids because solubility of samples increase with increasing the strength of the acid. Weak acids e.g: CH_3COOH, $H3PO_4$.

HF is used for the dissolution of silicate samples. When HF is used glass or porcelain equipments must not be used as HF will dissolve them because of the presence of silicon oxide.

$HClO_4$ and HNO_3 are strong acids and they are oxidizing agents as they convert metals into soluble acid oxides.

c. **Strong and Weak bases**.

d. **Fusion**: this process is used when the sample is insoluble in water, acids or bases, the sample is converted to a soluble substance by "fusion" which is a chemical reaction carried out at high temperature. In this process the sample is reacted with another compound to produce a product which is soluble in aqueous solution. The compound that is added to react with the sample is called a flux such as, $KHSO_4$, $Na2CO_3$.

Organic solvents are used for the dissolution of **organic samples**.

3. Initialization the reaction medium:

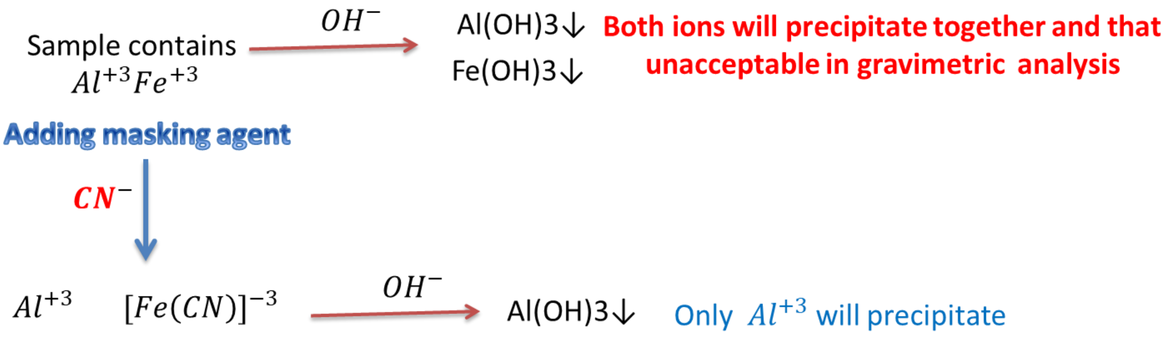
After the sample was dissolved we should initialize the reaction medium for the reaction between the analyte and precipitating agents and we should conceder these points

a. **Volume of the solution**: The volume must be suitable (50-200 ml) to minimize the solubility of precipitate formed later.

b. Solution temperature

c. pH of the solution should be suitable.

d. Removal of interferences: Interferences are materials present in the sample that have the same reaction, as the analyte, toward the precipitating agent. For example, Fe^{+3} interfere with Al^{+3} and Br^- interfere with Cl^- so, the interferences must be removed (separated) from the solution or must be converted into inactive form toward the reaction with the precipitating agent.



4. Precipitation:

Precipitation process involves the conversion of analyte quantitatively into a sparingly soluble substance called precipitate on the addition of a chemical reagent called precipitating agent.

Properties of precipitating reagents used in gravimetric analysis:

1. Unreactive with constituent of the atmosphere (H_2O, CO_2, O_2).
2. should be of known composition after it is dried or ignited.
3. should be pure (no impurities).
4. A small amount of analyte should yield a relatively large amount of precipitate.
5. should be selective for the analyte to avoid the effect of interference.

5. 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. During digestion at elevated temperature:

- **Small particles tend to dissolve and reprecipitate on larger ones.**
- **Individual particles agglomerate.**
- **Adsorbed impurities tend to go into solution.**

6. Filtering and Washing the Precipitate:

It is crucial to wash the precipitate very well in order to remove all adsorbed species which will add to weight of precipitate. One should be careful not to use too much water since part of the precipitate may be lost. Also, in case of colloidal precipitates we should not use water as a washing solution since peptization would occur. In such situations dilute nitric acid, ammonium nitrate, or dilute acetic acid may be used. Usually, coagulated particles return to the colloidal state if washed with water, a process called peptization.

Properties of the washing solution:

a- It should remove the impurities and the adsorbed ions and shouldn't react with the precipitate.

b- Washing solution should be volatile.

c- The washing solution shouldn't cause peptization (formation of colloidal precipitate).

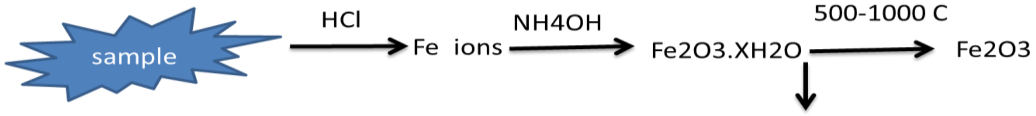
Peptization ⟶ increases the solubility of precipitate

Coagulation ⟶ decreases the solubility of precipitate

7. Drying or ignition of precipitates:

Drying is used for precipitates of well-known and stable chemical composition (100-110 oC) to remove the remaining water or washing solution.

Ignition is used for the not well known composition or unstable precipitates using muffle furnace (900-1000 °C).



8. Weighing of the precipitate using sensitive balance.

9. Calculations:

$$1-\ \text{gravimetric}\ factor = \frac{At.or\ molecular\ wt.of\ analyte}{molecular\ wt.of\ precipitate}$$

2- Weight of analyte = wt. of precipitate × gravimetric factor

$$3-\ \%\ of\ analyte = \frac{wt.of\ analyte}{wt.of\ sample} \times 100$$

$$g\backslash L\ \ of\ analyte = \frac{wt.of\ analyte}{Volume\ in\ ml\ of\ sample} \times 1000$$

$$\%\ \ analyte = \frac{wt.of\ precipitate \times \frac{At.or\ M.wt.of\ analyte}{M.wt.of\ precipitate}}{wt.of\ sample} \times 100$$

If our goal, determine the % of K2SO4 or investigate their purity of it

$$\boxed{K_2SO_4} + BaCl_2 \longrightarrow \boxed{BaSO_4\downarrow} + 2KCl$$

$$1-\text{gravimetric factor} = \frac{\text{At. or molecular wt. of analyte}}{\text{molecular wt. of precipitate}} = \frac{M.wt\ of\ K_2SO_4}{M.wt\ of\ BaSO_4}$$

2- Weight of analyte = wt. of precipitate × gravimetric factor

$$\text{Wt. of } K_2SO_4 = \text{Wt. of } BaSO_4 \text{ x } \frac{\text{M.wt. of } K_2SO_4}{\text{M.wt. of } BaSO_4}$$

$$3-\%\ \text{of analyte} = \frac{\text{wt. of analyte}}{\text{wt. of sample}} \times 100 \qquad \%\ K_2SO_4 = \frac{\text{wt. of } K_2SO_4}{\text{wt. of Sample}} \text{ x } 100$$

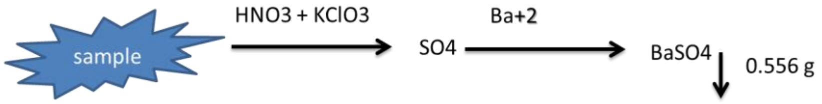
$$= \frac{\text{Wt. of } BaSO_4 \text{ X } \dfrac{\text{M.wt. of } K_2SO_4}{\text{M.wt. of } BaSO_4}}{\text{wt. of Sample}} \text{ x } 100$$

S analyte ⟶ $BaSO_4$ precipitate

$$\%\ S = \frac{\text{Wt. of } BaSO_4 \text{ X } \dfrac{\text{A.wt. of S}}{\text{M.wt. of } BaSO_4}}{\text{wt. of Sample}} \text{ x } 100$$

Example:

An ore is treated with Conc. HNO3 and KClO3 to convert all S to sulphate, the sulphate is then precipitated and weighed as BaSO4. What is the %S in an ore, 1.0 g of which yield 0.556 g BaSO4



1 g of sample contain S

1- Calculate the *gravimetric factor* $\quad \text{gravimetric factor} = \frac{\text{At. or molecular wt. of analyte}}{\text{molecular wt. of precipitate}}$

$$\text{gravimetric factor} = \frac{32}{233.4} = 0.1371$$

2- Calculate the weight of S in the sample from the weight of precipitate

Weight of analyte = wt. of precipitate × gravimetric factor

$$wt\ of\ S = \quad wt\ of\ BaSO4\ (0.556) x\ \ 0.1371 = 0.07623$$

3- Calculate the % of S in the sample $\quad \%\ \mathbf{of\ analyte} = \frac{\mathbf{wt.\ of\ analyte}}{\mathbf{wt.\ of\ sample}} \times \mathbf{100}$

$$\%S = \frac{0.07623}{1} \text{ x } 100 = 7.623$$

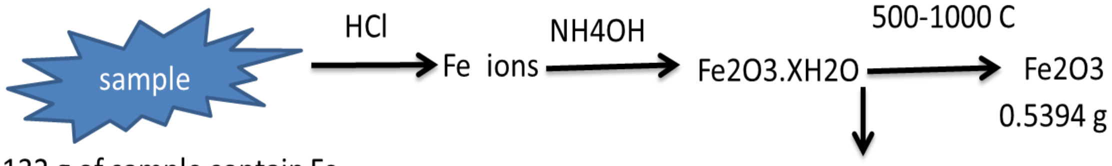
$$\%\ S = \frac{\text{Wt. of } BaSO_4 \text{ X } \dfrac{\text{A.wt. of S}}{\text{M.wt. of } BaSO_4}}{\text{wt. of Ore}} \text{ x } 100$$

$$= \frac{0.556 \times \dfrac{32}{233.4}}{1} \times 100$$

$$= \frac{0.556 \times 0.137}{1} \times 100 = 7.622$$

Example:

An ore was analysed by dissolving 1.132 g sample in concentrated HCl. The resulting solution diluted with water, and the iron III was precipitated as hydrous oxide Fe2O3.XH2O by the addition of NH3. After filtration and washing, the residue was ignited at a high temperature to give 0.5394 g of pure Fe2O3 calculate a-the %Fe and b-the % Fe3O4 in the sample. At.wt. Fe=55.85, O=16.



1.132 g of sample contain Fe

1- Calculate the $gravimetric\ factor$ 1- Calculate the $gravimetric\ factor$

$$gravimetric\ factor = \frac{2x\ 55.85\ (A.wt\ of\ Fe)}{159.7\ (M.wt\ of\ Fe2O3)} = 0.699$$

2- Calculate the weight of Fe in the sample from the weight of precipitate

$$gravimetric\ factor = \frac{2x\ 55.85\ (A.wt\ of\ Fe)}{159.7\ (M.wt\ of\ Fe2O3)} = 0.699$$

$$wt\ of\ Fe = \quad wt\ of\ Fe2O3\ (0.5394)x\ \ 0.699 = 0.377$$

3- Calculate the % of S in the sample $wt\ of\ Fe = \quad wt\ of\ Fe2O3\ (0.5394)x\ 0.699 = 0.377$

$$\%S = \frac{0.377}{1.132} \text{ x } 100 = 33.3\%$$

Or

$$\%\ Fe = \frac{\text{Wt. of ppt.}(Fe_2O_3) \text{ x Grav. factor}}{\text{wt. of Sample}} \text{ x } 100$$

$$\%\ Fe = \frac{0.5394 \ \ X\ \frac{2 \text{ x A.wt. Fe}}{\text{M.wt. of } Fe_2O_3}}{1.132} \text{ x } 100$$

$$\%\ Fe = \frac{0.5394 \ \ X\ \frac{2 \text{ x } 55.85}{159.7}}{1.132} \text{ x } 100$$

$$= \frac{0.3772}{1.1329} \times 100 = 33.3\%$$

1- Calculate the $gravimetric\ factor$ $\quad gravimetric\ factor = \frac{At.or\ molecular\ wt.of\ analyte}{molecular\ wt.of\ precipitate}$

$$gravimetric\ factor = \frac{2x\ 231.55\ (M.wt\ of\ Fe3O4)}{3x\ \ 159.7(M.wt\ of\ Fe2O3)} = 0.967$$

2- Calculate the weight of Fe in the sample from the weight of precipitate

Weight of analyte = wt. of precipitate × gravimetric factor

$$wt\ of\ Fe3O4 = \quad wt\ of\ Fe2O3\ (0.5394)x\ \ 0.966 = 0.521$$

3- Calculate the % of S in the sample $\quad \%\ of\ analyte = \frac{wt.of\ analyte}{wt.of\ sample} \times 100$

$$\%Fe3O4 = \frac{0.521}{1.132}\ \text{x}\ 100 = 46.04\%$$

$$\%\ Fe_3O_4 = \frac{\text{Wt. of }(Fe_2O_3)\ X\ \frac{2\ x\ \text{M.wt. of }Fe_3O_4}{3\ x\ \text{M.wt. of }Fe_2O_3}}{\text{wt. of Sample}}\ \text{x}\ 100$$

$$\%\ Fe_3O_4 = \frac{0.5394\ \ X\frac{2\ (3x55.85+4\ x\ 16}{3(2\ x55.85+3\ x16)}}{1.132}\ \text{x}\ 100$$

$$= \frac{0.52138}{1.1329} \times 100 = 46.04\%$$