National University –SUDAN

Faculty of Clinical and Industrial Pharmacy

Second Year (**Batch-PA-14**)-Semester Four

Professional Skills-2- Laboratory Skills-1

(**PA-SKILL-221**)

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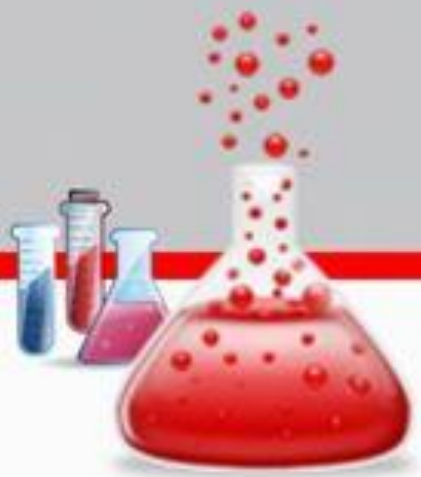

Precipitation

Gravimetric Analysis

- A Gravimetric analysis is based upon the measurement of the weight of a substance that has
- a known composition and
- chemically related to the analyte.
- P = Ag_3PO_4

Advantages

- Accurate and precise.
- Possible sources of errors can be checked.
- It is an ABSOLUTE method.
- Relatively inexpensive

Disadvantages

Careful and time consuming.

Scrupulously clean glassware.

Very accurate weighing.

Coprecipitation.

Types of gravimetric analysis

- Volatilisation methods.
- Precipitation methods.

VOLATILISATION METHODS

Antacid preparation

Carbonate and bicarbonate

The total amount of carbonate in whatever form is found by placing the analyte in a solution containing an excess of H_2SO_4.

- This solution is in a flask connected to incoming nitrogen gas gently bubbled through the solution and an exit tube first to a drying agent to absorb aerosolized water and water vapour and then to a mixture of NaOH and drying agent to absorb the CO_2 and water subsequently produced by the absorption by NaOH.

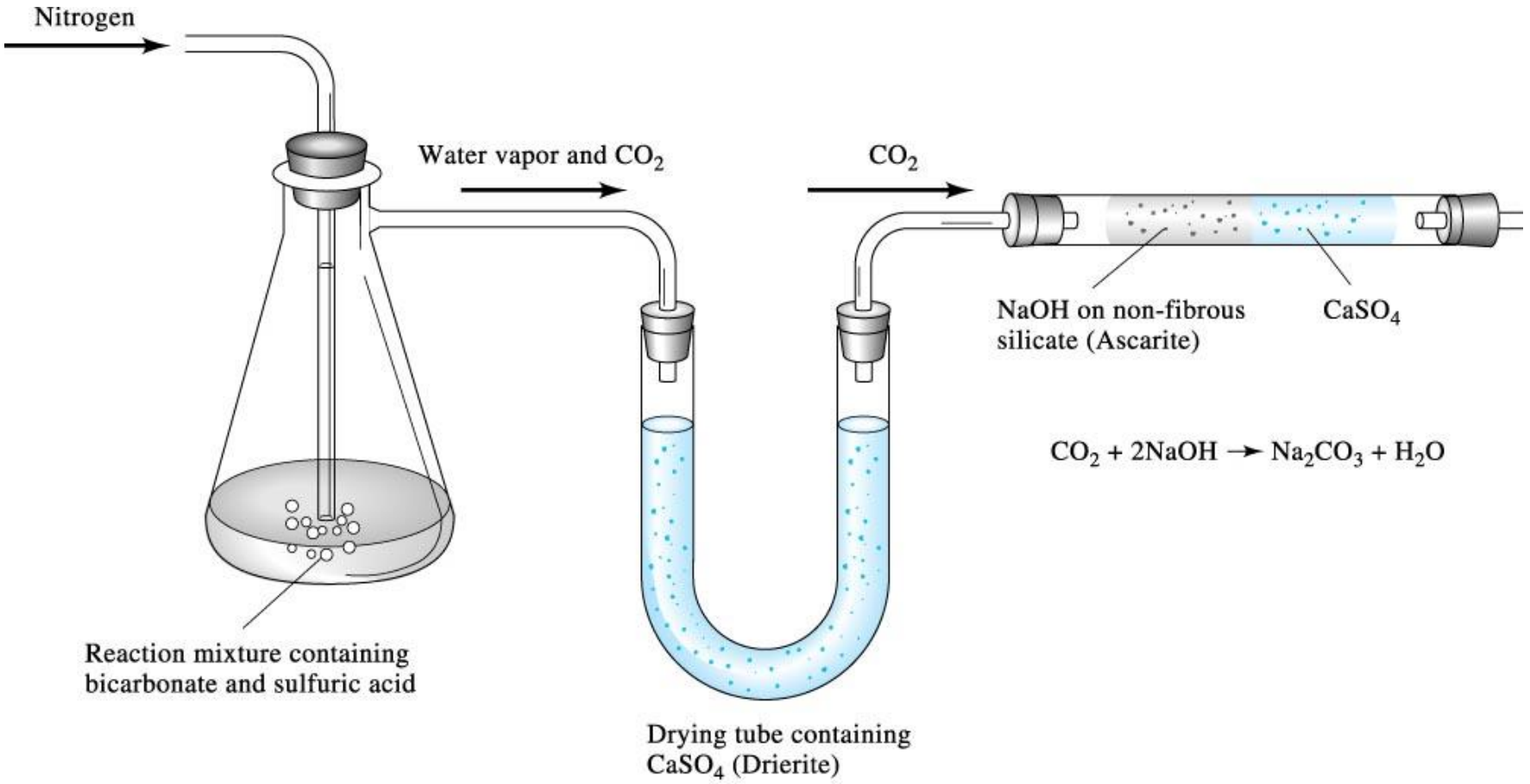

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Fig 12-8, p.333

Volatilization Method

- Reactions
- $NaHCO_3+H_2SO_4 \rightarrow CO_2+H_2O+NaHSO_4$
- In the adorbent the reaction is:
- $CO_2+2NaOH \rightarrow Na_2CO_3+H_2O$
- Weigh the adsorbent before and after the reaction
- Find the weight of Na_2CO_3

Precipitation methods

- In precipitation methods, the species to be determined is precipitated by a reagent that yields a sparingly soluble product that has a known composition or can be converted to such a substance.

The precipitation method

- Steps
- Preparation of the Solution
- Precipitatation of the analyte from solution
- Digestion and filteration
- Drying
- Weighing the solid on an analytical balance
- Calculation of the analyte concentration in the original solution based on the weight of the precipitate.

Conditions for analytical precipitation

1. The precipitate should also be "insoluble“
2. an analytical precipitate should consist of perfect crystals large enough to be easily washed and filtered.
3. free from impurities and be large enough so that it presented a minimum surface area onto which foreign ions could be adsorbed.

Precipitating agents

These can be inorganic such

as nitric acid, ammonia, hydrogen sulphide, sulphuric acid, hydrochloric acids, silver nitrate and barium chloride

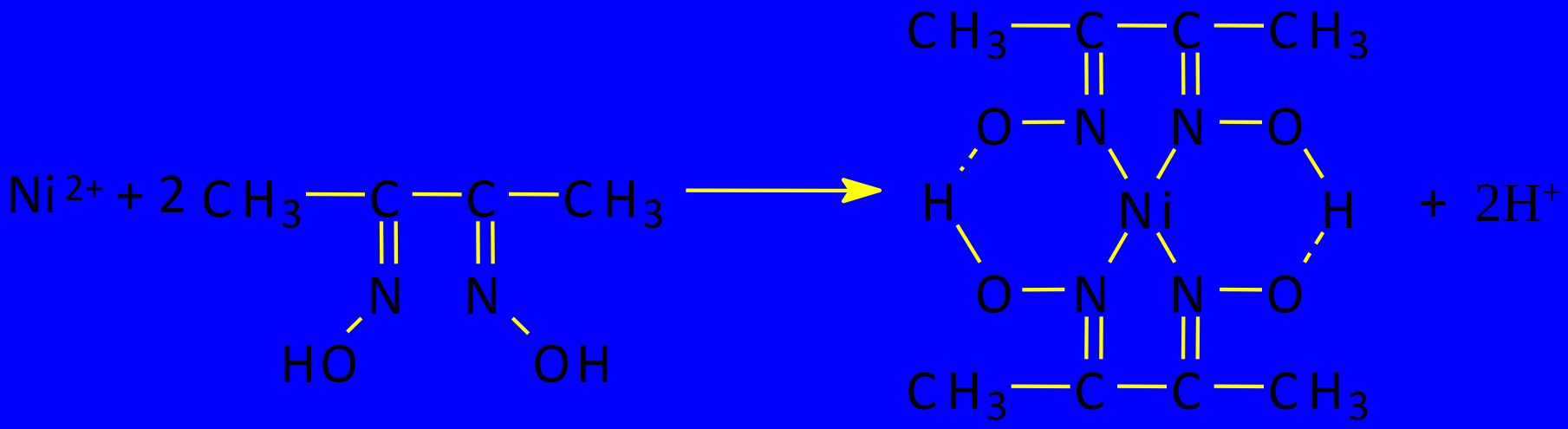
OR organic as tabulated below.

Organic precipitating agents

Compound	Ions precipitated
Dimethylglyoxime	Ni^{2+},Pd^{2+},Pt^{2+}
EDTA	Zn^{2+}, Cu^{2+}, Pb^{2+}, Ca^{2+}, Ni^{2+}, Fe^{3+}
Cupferron	$Fe^{3+,}$ Zr^{4+},Ce^{4+},Ga^{3+},Sn^{4+}
8-Hydroxyquinoline	Fe^{3+},Al^{3+},Mg^{2+},Zn^{2+}, Cu^{2+},Cd^{2+},Pb^{2+}, Bi^{3+}, Ga^{3+},Th^{4+}, Zr^{4+}, TiO^{2+}, UO_2^{2+}
Salicylaldoxime	Bi^{3+},Ni^{2+},Pd^{2+},Zn^{2+}, Cu^{2+},Pb^{2+}
1-Nitroso-2-naphthol	Fe^{3+},Co^{2+},Pd^{2+}, Zr^{4+}
Nitron ($C_{20}H_{16}N_4$)	NO_3^-, ClO_4^-, BF_4^-, WO_4^{2-}
Sodium tetraphenylborate	NH_4^+, Ag^+, Cs^+, Rb^+, K^+
Tetraphenylarsonium chloride	$Cr_2O_7^{2-}$, MnO_4^-, MoO_4^{2-},WO_4^{2-},

Gravimetric Analysis

- Dimethylglyoxine



- Weakly alkaline conditions
- Nickel salt bright red

Steps in a Gravimetric Analysis

- **Preparation of the Solution**
- This may involve several steps including adjustment of the pH of the solution in order for the precipitate to occur and get a precipitate of desired properties.
- removing interferences.

The factors that determine the particle size

- Precipitate solubility (S)
- Reagent concentration (Q)
- Temperature
- The rate of mixing the analyte with the precipitating agent.

Relative Supersaturation

- **Relative Supersaturation = (Q – S)/S**
- Particle size seems to be inversely proportional to Relative Supersaturation
- For the best possible results, conditions need to be adjusted such that Q will be as low as possible and S will be relatively large.

Minimization

The following methods are used to approach these criteria.

Precipitation from hot solution (Increase S)

Precipitation from dilute solution (Decrease Q)

Slow addition of the reagent

Precipitation at low pH (increase S)

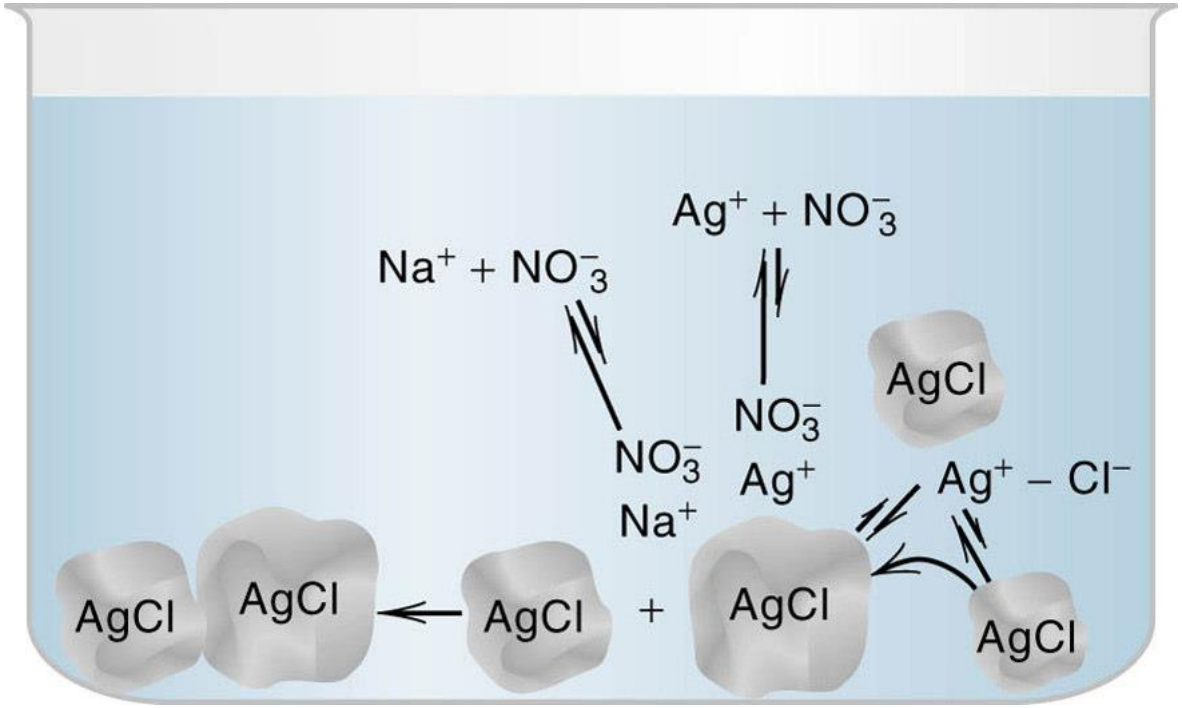
Digestion of the precipitate (improve crystallization)

Steps in a Gravimetric Analysis

- 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.

3. Digestion of the Precipitate

- a process which involves heating the solid and mother liquor for a certain period of time. During digestion, small particles dissolve and larger ones grow.



4. Washing and Filtering the Precipitate

- One should be careful nor 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 (i.e return to small particles) would occur. In such situations dilute nitric acid, ammonium nitrate, or dilute acetic acid may be used.

5. Drying and Ignition

- The purpose of drying (heating at about 120-150 ^{o}C in an oven) or ignition in a muffle furnace at temperatures ranging from 600-1200 ^{o}C is to get a material with exactly known chemical structure so that the amount of analyte can be accurately determined.
- Drying and ignition.
  - Removes solvents and volatiles
  - Decomposition to known form

6. Weighing the solid

- Use a sensitive balance
- Frequently the constituent being estimated is weighed in a form other than that it was precipitated in.

- Mg^{2+}: precipitated as $Mg(NH_4)PO_4.6H_20$ but is weighed as magnesium pyrophosphate $Mg_2P_2O_7$ after ignition.

Impurities in Precipitates

- **Occlusion (trapped water, solvent):**
- Some constituents of the precipitation medium may be trapped in the crystal structure.
- The trapped materials can be water, analyte ions, precipitating agent ions, or other constituents in the medium.
- Slow addition of precipitating agent and stirring may avoid occlusion but if it does occur, dissolution of precipitate and repracipitation may have to be done.

Impurities in Precipitates

Inclusion:

If the precipitation medium contains ions of the same charge and size as one forming the crystal structure of the precipitate, this extraneous ion can replace an ion from the precipitate in the crystal structure.

Impurities in Precipitates

- **Inclusion:**
- For example, in the precipitation of NH_4MgPO_4 in presence of K^+ ammonium leaves the crystal magnesium ammonium phosphate and is replaced by K^+ since both have the same charge and size. However, the FW fro NH_4^+ is 18 while that of K^+ is 39. In this case a positive error occurs as the weight of precipitate will be larger when K^+ replaces NH_4^+. In other situations we may get a negative error when the FW of the included species is less than the original replaced species.

Impurities in Precipitates

- **Surface Adsorption**:
- The adsorption discussed earlier always results in positive errors in gravimetric procedures

Impurities in Precipitates

- **Postprecipitation:**
- In cases where there are ions other than analyte ions which form precipitates with the precipitating agent but at much slower rate than analyte.
- and if the precipitate of the analyte is left for a long time without filtration then the other ions start forming a precipitate over the original precipitate leading to positive error.

Gravimetric Factor

- The relationship between the analyte and the final product is called gravimetric factor (GF)
- GF=(a/b)xMwt of analyte/Mwt of product
- a= moles of the analyte
- b= moles of the product

Example

- Calculate the grams analyte to mg precipitate for the following: P (at wt =30.97) in Ag_3PO_4 (FW = 711.22),
- **Solution**
- P = Ag_3PO_4
- mmol p = mmol Ag_3PO_4
- mg P/30.97 = mg Ag_3PO_4/711.22
- mg P/mg Ag_3PO_4= 30.97/711.22 = 0.04354

Example

-
- Calculate the grams analyte to mg precipitate for the following: Bi_2S_3 (FW 514.15) in $BaSO_4$ (FW = 233.40)
- **Solution**

- $Bi_2S_3 = 3\ BaSO_4$
- mmol Bi_2S_3 = 1/3 mmol $BaSO_4$
- mg Bi_2S_3/FW Bi_2S_3 = 1/3 mg $BaSO_4$/FW $BaSO_4$
- mg Bi_2S_3/514.15 = 1/3 mg $BaSO_4$/233.40
- mg Bi_2S_3/ $BaSO_4$ = **1/3** (514.15/ 233.40) = 0.73429

Objectives

By the end of this lesson the student is expected ……..

1- To Define precipitation
2- To determine factors affecting on precipitation
3- To practice on an experiment of precipitation practically

Precipitation

- Precipitation is the creation of a solid from a solution. When the reaction occurs in a liquid solution, the solid formed is called the 'precipitate'. The chemical that causes the solid to form is called the 'precipitant'. Without sufficient force of gravity (settling) to bring the solid particles together, the precipitate remains in suspension.

- Sometimes the formation of a precipitate indicates the occurrence of a chemical reaction. If silver nitrate solution is poured into a solution of sodium chloride, a chemical reaction occurs forming a white precipitate of silver chloride. When potassium iodide solution reacts with lead(II) nitrate solution, a yellow precipitate of lead(II) iodide is formed.

Factors affecting precipitation

- Precipitation may occur if the concentration of a compound exceeds its solubility (such as when mixing solvents or changing their temperature). Precipitation may occur rapidly from a supersaturated solution.

- In solids, precipitation occurs if the concentration of one solid is above the solubility limit in the host solid, due to e.g. rapid quenching or ion implantation, and the temperature is high enough that diffusion can lead to segregation into precipitates. Precipitation in solids is routinely used to synthesize Nano clusters.
- An important stage of the precipitation process is the onset of nucleation. The creation of a hypothetical solid particle includes the formation of an interface, which requires some energy based on the relative surface energy of the solid and the solution. If this energy is not available, and no suitable nucleation surface is available, supersaturation occurs.

Applications of precipotation

- Crystals of meso-tetratolylporphyrin from a reflux of propanoic acid precipitate on cooling

- Copper from a wire is displaced by silver in a silver nitrate solution it is dipped into, and solid silver precipitates out.
- Precipitation reactions can be used for making pigments, removing salts from water in water treatment, and in classical qualitative inorganic analysis.

- Precipitation is also useful to isolate the products of a reaction during workup. Ideally, the product of the reaction is insoluble in the reaction solvent. Thus, it precipitates as it is formed, preferably forming pure crystals. An example of this would be the synthesis of porphyrins in refluxing propionic acid. By cooling the reaction mixture to room temperature, crystals of the porphyrin precipitate, and are collected by filtration

IT'S A SLOW PROCESS, BUT QUITTING WON'T SPEED IT UP.