# **II- QUANTITATIVE ANALYSIS**

Classical quantitative analysis methods are divided into two parts:

1. Gravimetry

2. Volumetry

The specific amount weighing from the material to be analyzed is dissolved by the appropriate method. The resulting solution is complete to a certain volume. Analysis is carried out by taking a certain amount of this solution.

#### **1. GRAVIMETRY**

Gravimetry is based on weighing only after converting the substance to be analyzed directly into a solid or a dissolving compound. In addition this, some compounds like that  $H_2O$ ,  $CO_2$  etc. can be determined by means of calculated loosing amounth of total weight.

The determined ion present in the solution is precipitated as a poorly soluble compound with a suitable reagent. The precipitate is digested, filtered, washed, dried and ignited, weighed.

## 1.1. Precipitation

During precipitation, the amount of residue in the solution should be less than the minimum amount that an analytical balance can weigh, less than 0,0001 g.

The type of precipitate should be suitable filtration and can be washed quickly. For this reason the precipitates in the crystal structure is wanted to be big granule. Because, if the precitate get big, it can be block the pore of filter paper or can pour the pore. In addition, unwanted ions are more adsorbed in the solution as the total surface increases.

After the precipitating substance is dried and ignited, the composition should be converted into a precise substance.

To complete the precipitation, the precipitating reagent should be added in an amount of 5-10% from the required amount. Participation of the excess of the reagent should be disadvantageous in some cases to cause the redeposition of the precipitate to be resolved, as well as to cause adsorption of the precipitate to contaminate the precipitate.

Excessive amounts of foreign ions in the solution should increase the solubility and not work in a concentrated environment.

Precipitates are crystallized or amorphous. To ensure that the crystals are coarse in the formation of crystallized precipitates and to prevent oversaturated solutions from forming:

1) The precipitation sufficiently diluted solution should be made by slow addition of the diluted reagent.

2) In order to avoid local over concentration, the addition of reagent should be done by mixing.

3) In order to slow down the crystal formation, precipitation must be done in the hot and complete by the addition of excess of reagent.

When amorphous precipitates are formed by coagulation of colloidal solutions, precipitation is occurred by heating the colloidal solutions or adding the coagulating electrolyte.

The amorphous Fe(OH)<sub>3</sub>, Al(OH)<sub>3</sub> precipitates obtained from the dilute solutions are loose and bulky. They adsorb unwanted ions because of their surface area.

Amorphous precipitates should be small grains, unlike crystallized precipitates. Because the smaller particles are easier to collapse and adsorbs less foreign matter.

For this purpose, the solution should be concentrated in the amorphous precipitate formation, the process should be done in the hot.

After the sedimentation is complete, approximately 100 mL of water should be added to the medium and immediately filtered, as the amount of foreign matter adsorbable in the concentrated medium increases.

Precipitation is carried out in a selected beaker filled to the maximum of 2/3 of the cabinet at the end of the total volume treatment. The addition of the precipitation reagent is done with burette, pipette and occasionally gauge vessel. Mixing is usually done with a bagel 3-4 cm longer than the beaker's height. Mechanical or magnetic stirrer is used for long mixing time.

## **1.2. Digestion**

The precipitates in the crystal structure usually do not leak immediately. In its own case or in the water bath, it is left for 3-4 hours or overnight. This process is called maturation.

During precipitation, large crystals as well as very small crystals occur. The solubility of small crystals is higher than that of large crystals. Small crystals dissolve during standby. On the surface of larger crystals accumulation occurs and large crystals are obtained.

In addition to facilitating filtration, Digestion also allows precipitation to be purified.

#### 1.3. Filtration

The black tape has large size pores, and the paper symbols. The filter paper is inserted well into the hopper dry. The air bubbles between the funnel and the paper are removed when the distill is filled with water and is expected to be filtered. The droplet of dripping filtrate is placed in contact with the edge of the beaker.

The filtered liquid is carefully transferred to the filter paper without initially mixing to prevent plugging of the pores. To prevent material loss by splashing, the drained fluid is transferred from the beaker in the beaker onto a bagel which is held in the middle of the funnel but does not come into contact with the funnel. The filter paper should not be completely filled with liquid. It should be 5 mm below the upper edge of the paper. After the entire liquid is transferred to the filter paper.

The precipitate should not cover more than half of the filter paper. Otherwise it can not be washed well.

Filters outside the paper are used to filter precipitates that are easily reduced during heating or only weighed by drying.

## 1.4. Washing

On the surface of the precipitate, washing is carried out to remove foreign ions adsorbed and the main solvent.

In the case of washing with pure water, depending on the structure of the precipitate, losses may occur due to dissolution, colloidal formation and hydrolysis. Washing solutions are used to prevent this.

Washing solutions are collected in three groups:

1) Solvents that precipitate in water to dissolve by ionization: These are solutions containing common ions with the precipitate. The co-ion can easily be given in the form of a solution of a volatile compound or precipitate.

For example, the Fe(OH)<sub>3</sub> precipitate can be washed with the NH<sub>4</sub>OH solution.

2) Solvents that prevent the dissolution of precipitate by giving colloidal solution: When precipitation is provided by the addition of coagulant, this electrolyte is removed during washing with water and the colloidal solution comes back to the water. In this case, washing is

carried out with dilute electrolyte solution. During washing, the ions contained in the wash solution are replaced by foreign ions adsorbed by the precipitate. For this purpose, the ammonium salt, acid dissolving, etc. used. For example, Fe(OH)<sub>3</sub>, ammonium salt solution; AgCl is washed with 1% HNO<sub>3</sub> solution.

3) Solvents which inhibit the hydrolysis of the precipitate: Some precipitates are lost in water washing due to hydrolysis. For example, magnesium ammonium phosphate precipitate,

 $MgNH_4PO_4 + H_2O \rightleftharpoons MgHPO_4 + NH_4OH$ 

In the form of hydrolysis. NH<sub>4</sub>OH is added to the wash water to prevent this.

If the formation of ionizing colloidal solution is not lost due to reasons such as hydrolysis, it is washed with distilled water.

## Washing process:

In the filter wash, a certain amount of washing solution or distilled water is added to the precipitate. Once all of this has been filtered, another portion is added. The same volume is more effective than using washing liquid in small portions.

In another wash, the precipitate is taken up in a beaker and a certain amount of washing liquid is added thereto, followed by stirring. After the sediment is settled to the bottom of the beaker, filtration is carried out. This method is more effective in eliminating pollution since foreign substances in the sediment dissolve to the fullest extent.

In both washings, the washing is continued until the foreign matter desired to be purified from the precipitate is not found in the filtrate.

If the solubility of the precipitate is low, the hot liquid is preferred in washing, since it will increase the solubility of the foreign substances and the filtration will be faster due to the decrease in viscosity.

## **1.5. Drying and Igniting**

The washed precipitate is washed with water or the like before weighing. It is dried or pissed to get the volatile substances out. During the glow process, the composition of the precipitate may remain the same or change. For example, while the structure of  $BaSO_4$  remains the same in the glow process, the MgNH<sub>4</sub>PO<sub>4</sub> precipitate turns into Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub> form. If the required temperature is less than 250 °C, the drying process is irritating if it is between 250 and 1200 °C. The drying

process is carried out in the body, the glowing oven or the burner. Dried sediment is filtered through filter paper, Gooch crucible, sintered glass or die bore porous porcelain crucible.

If the precipitate is incinerated, filter paper, dia pore porcelain or silica crucible or Munroe crucible is used for filtration.

Fixed scales are brought to the crucible before drying or glowing. For this, the crucible is heated at the drying or glowing temperature. It is cooled and weighed by taking the desiccator with the help of a pliers or wire tongs. The crucible is reheated and weighed. If the difference between the two weights does not exceed 0,0001 g, it is assumed that the croissant has reached a fixed level of digestion. Otherwise, the process is repeated.

When filtration is done using strainer paper, the edges are folded with the help of a moist strainer paper pens and then the crucible is brought to a fixed weighing scraper so that the sharp tip remains at the top. The crucible is first placed obliquely on the asbestos wire with clay triangle. The crucible is occasionally twisted and the filter paper is heated to dryness. After the drying is completed, the asbestos wire is lifted and the paper is heated by heating directly in the flame. At this time, either the crucible is heated from the side or it is placed obliquely on the clay triangle to provide the necessary air flow for combustion. If the paper flames during the burning, the crucible is turned off by flicking it with the watch glass. After stopping the smoke outlet, put the crucible metal oven tongs in the constant temperature ash furnace and heat it for 12-15 minutes.

It is cooled and weighed by taking the desiccator with wire tongs or pens again. Coke is reheated and weighed with the substance. If the difference between the two weights does not exceed 0.0001 g, it is assumed that the weight is constant. Otherwise, the glowing and weighing process is repeated.

Note: 1) After the drying and burning process, the crucible should not be held until weighing.

2) If the substance to be weighed is excessive moisture, the cover is used between cooling and weighing.

### 1.6.Weighing

In gravimetric analysis, weighing is carried out on a double or single-pan balance with a sensitivity of at least 0.0001 grams. It is recommended to weigh empty and full crucible on the same balance. During material weighing, since there will be difference between full and empty crucible, there will be no error from the balance.

During weighing:

- 1. Non-cooled crucible should not be put on the balance.
- 2. The lids should be closed before the balance is turned to the weighing position.
- 3. First, approximate weigh should be found in rough weighing position, and then sensitive weighing should be carried out.
- 4. When the balance is in weighing position, the crucible should not be put on or taken to the pan.
- 5. Before weighing, the balance is checked whether it is at zero level (balanced) or not and it should be adjusted if necessary.
- 6. Whether the bottom of the balance is properly in a horizontal position should be controlled from water level on the balance.
- In the balance, there should be desiccant substances such as silica gel, anhydrous CaCl<sub>2</sub>, NaOH and so on.

## **1.7. Calculation of Result**

In the calculation of the result, regardless of the steps followed during the analysis, it is sufficient to use only the sought and weighed substance formulas. It is recommended that the amount of substance to be weighed is 0.1-0.5 g. The increase in the amount of the substance reduces the error rate in the analysis. When writing the calculated result, the last digit should be the first suspected number. In the student laboratory, four numbers after the comma should be written.

Example: For the determination of sodium sulphate, the sulphate in solution is precipitated by adding BaCl<sub>2</sub> solution. After it is filtered and washed, it is weighed by heating. In BaSO<sub>4</sub> weighing, if T is gram, the amount of sulphate in the solution is calculated as follows:

Crucible weight with precipitate - empty crucible weight = T (amount of BaSO<sub>4</sub>)

While;

233 g BaSO<sub>4</sub> is formed by 142 g Na<sub>2</sub>SO<sub>4</sub> T g BaSO<sub>4</sub> is formed by X g Na<sub>2</sub>SO<sub>4</sub>  $\overline{X = \frac{142}{233} \times T} g Na_2SO_4$ 

Formerly, 142/233 ratio in the equation obtained as a result of ratio is called gravimetric factor and these values took place in analytical chemistry charts. This equation, which is basically expressed as a formula, is the result of a simple ratio and it is not necessary to be used by memorizing.

#### **1.8. Iron-Manganese Separation**

One of the important processes in the analysis of glass, cement, mineral, alloy etc. is the separation of divalent cations from higher valence cations. In this separation, it is benefited from the fact that the precipitation pHs of the metal hydroxides are different. The precipitation pHs of some metal-hydroxides are given in the following table:

pН	Metal Ion
2	Ti <sup>4+,</sup> Zr <sup>4+</sup>
3	${\rm Sn}^{2+}, {\rm Fe}^{3+}$
4	Th <sup>4+</sup>
5	$Al^{3+}$
6	$Zn^{2+}, Cu^{2+}, Cr^{3+}$
7	Fe <sup>2+</sup>
8	$Co^{2+}, Ni^{2+}, Cd^{2+}$
9	$Ag^{+}, Mn^{2+}, Hg^{2+}$
11	$Mg^{2+}$

In the analysis reports, the metal oxide mixture weighed after the hydrocarbons of  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$  cations are separated and heated is given as  $R_2O_3$ .

For separation by precipitation in the form of hydroxide, weak bases are used. Ammonium hydroxide, acetate and benzoate salts, urea, pyridine, urotropine are used as weak bases. Ammonium hydroxide and acetate salts among them are widely used. As ammonium hydroxide may contain carbonate and silicate, it causes divalent cations to precipitate partially.

Furthermore, if it is not added to the medium, pH rising causes aluminum hydroxide to precipitate as aluminate. Such problems are not seen in precipitation by acetate.

Since the metal hydroxides, which are precipitated by weak bases, are voluminous and gelatinous, they adsorb ions in the solution. For this reason, it is recommended to filter and dissolve the solution in acid, to precipitate it again and to combine the filtrates.

This method will be applied in the student laboratory since ammonium hydroxide precipitation is used more often.

During the precipitation of  $Fe^{3^+}$  ions with NH<sub>4</sub>OH, other cations precipitated in the form of hydroxides are also separated together. For example;  $Al^{3^+}$ ,  $V^{3^+}$ ,  $Ti^{4^+}$ ,  $Zr^{4^+}$  and so on. The medium should be buffered by adding the ammonium salt to prevent the precipitation of ions such as  $Mg^{2^+}$ ,  $Mn^{2^+}$ ,  $Zn^{2^+}$  and so on, which precipitate in the form of hydroxides at relatively high ph. Since NH<sub>4</sub>Cl will cause iron loss by forming volatile FeCl<sub>3</sub> during heating, NH<sub>4</sub>NO<sub>3</sub> should be used instead of NH<sub>4</sub>Cl or precipitation should be thoroughly washed with NH<sub>4</sub>NO<sub>3</sub>solution. If  $Al^{3^+}$  ion is present in the medium, it should be avoided to add excess NH<sub>4</sub>OH in order to separate it quantitatively with Fe<sup>3+</sup> in the form of hydroxide. Because it causes Al(OH)<sub>3</sub> to partially dissolve in aluminate form. Furthermore, the presence of substances such as hydroxyl acids, polyalcohols, phosphates, fluorides and so on, which complexes with Fe<sup>3+</sup> prevents the quantitative precipitation of iron.

## 1.9. Gravimetric Determination of Iron

Take your sample which is provided in a 100 mL volumetric flask and add distilled water till the its mark. Shake the solution well and transfer 25.0 mL of sample solution with pipette into a beaker. Add about 100 mL of distilled water and heat the solution on a hot plate to about 90-100°C. Boiling the solution must be avoided since it is possible to lose some of the solution through spattering. However, it is necessary to keep the solution at an elevated temperature in order to facilitate the formation of large, filterable particles and to minimize coprecipitation of foreign ions. After boiling gently for 1 min, add diluted NH<sub>4</sub>OH solution (1:1, v/v) dropwise until pH reaches 7 in order to precipitate Fe<sup>3+</sup> ions in the form of Fe(OH)<sub>3</sub>. Allow the precipitate to settle, and test for completeness of precipitation by adding a few more drops of NH<sub>4</sub>OH. If you detect the appearance of some red-brown precipitate as the drop of the solution moves downward through the solution add an additional NH<sub>4</sub>OH solution (control the pH.) The reaction is:

 $Fe(H_2O)_6^{3+} + 3 NH_3 \longrightarrow Fe(H_2O)_3(OH)_3 + 3 NH_4^+$ 

in simple terms;

 $Fe^{3+} + 3 NH_4OH$   $Fe(OH)_3 + 3 NH_4^+$ 

Decant the supernatant liquid through a black band filter paper. Wash the precipitate several times with hot 1% NH<sub>4</sub>NO<sub>3</sub> solution (The filtrate must be kept for determination of manganese). Remove the filter paper with precipitate and then place it in a crucible taken to

the constant weight. Dry the paper with a small flame and heat the crucible for 15 min at 500 - 550 °C on an electric furnace for ignition. Allow to coll in a desiccator and weigh Fe<sub>2</sub>O<sub>3</sub>.

$$2 \operatorname{Fe}(OH)_3 \longrightarrow \operatorname{Fe}_2O_3 + 3 \operatorname{H}_2O$$

Note: Total iron in the sample must be in the form of  $Fe^{3+}$  If not, 1-2 mL of con. HNO<sub>3</sub> or H<sub>2</sub>O<sub>2</sub> are added to the sample and so iron is oxidized.

# **Calculations:**

 $Fe^{3+} + 3 \text{ NH}_4\text{OH} \longrightarrow Fe(OH)_3 + 3 \text{ NH}_4^+$ 2 Fe(OH)\_3  $\longrightarrow$  Fe<sub>2</sub>O<sub>3</sub> + 3 H<sub>2</sub>O

 $T (Fe_2O_3) = m_{crucible with precipitate} - m_{crucible}$ 

T g Fe<sub>2</sub>O<sub>3</sub> . <u>1 mol Fe<sub>2</sub>O<sub>3</sub></u> . <u>2 mol Fe<sup>3+</sup></u> . <u>56 g Fe<sup>3+</sup></u> . <u>100 mL</u> 160 g Fe<sub>2</sub>O<sub>3</sub> 1 mol Fe<sub>2</sub>O<sub>3</sub> 1 mol Fe<sup>3+</sup> 25 mL = <u>112</u> **X** T X 4 g Fe<sup>3+</sup>/100 mL

## **II. Solution Route:**

 $T \; (Fe_2O_3) = m_{crucible \; with \; precipitate} \text{ - } m_{crucible}$ 

While,

160 g 
$$Fe_2O_3$$
is formed by  $2x56$  g  $Fe^{3+}$ (Fe: 56 g/mol)T g  $Fe_2O_3$ is formed by A g  $Fe^{3+}$ (Fe $_2O_3 : 160$  g/mol)

$$A = \frac{112}{160} \times T g F e^{3+}$$

While,

25 mL of sample	contain A x $10^3$ mg Fe <sup>3+</sup>
100 mL of sample	contain ? mg $Fe^{3+}$

The result is found as mg/100 mL

## 1.10. Gravimetric Determination of Manganese

Add 4 spoon of NH<sub>4</sub>Cl ve 2 spoon of  $(NH_4)_2HPO_4$  to the previous filtrate. Heat the solution to 90 – 95 °C and then add diluted NH<sub>4</sub>OH (1:3, v/v) until pH is 9. Continue to heat for a while and settle it on the water bath for 1-2 h for digestion.

 $Mn^{2+} + HPO_4^{2-} + NH_4OH \longrightarrow MnNH_4PO_4.H_2O$ 

Filter through a blue band filter paper. Wash the precipitate several times with cold 1%  $NH_4NO_3$  solution. Remove the filter paper with precipitate and then place it in a crucible taken to the constant weight. Dry the paper with a small flame and heat the crucible for 15-20 min at 700 – 800 °C on an electric furnace for ignition. Allow to coll in a desiccator and weigh  $Mn_2P_2O_7$ .

2 MnNH<sub>4</sub>PO<sub>4</sub>.H<sub>2</sub>O  $\longrightarrow$  Mn<sub>2</sub>P<sub>2</sub>O<sub>7</sub> + 2NH<sub>3</sub> + 3H<sub>2</sub>O

**Calculations:** 

 $Mn^{2+} + HPO_4^{2-} + NH_4OH \longrightarrow MnNH_4PO_4.H_2O$ 

2 MnNH<sub>4</sub>PO<sub>4</sub> . H<sub>2</sub>O  $\longrightarrow$  Mn<sub>2</sub>P<sub>2</sub>O<sub>7</sub> + 2 NH<sub>3</sub> + 3 H<sub>2</sub>O

 $T (Mn_2P_2O_7) = m_{crucible with precipitate} - m_{crucible}$ 

T g Mn<sub>2</sub>P<sub>2</sub>O<sub>7</sub> . <u>1 mol Mn<sub>2</sub>P<sub>2</sub>O<sub>7</sub></u> . <u>2 mol Mn<sup>2+</sup></u> . <u>55 g Mn<sup>2+</sup></u> . <u>100 mL</u> 284 g Mn<sub>2</sub>P<sub>2</sub>O<sub>7</sub> 1 mol Mn<sub>2</sub>P<sub>2</sub>O<sub>7</sub> 1 mol Mn<sup>2+</sup> 25 mL =  $\frac{110}{284} \times T_X 4 \text{ g Mn}^{2+}/100 \text{ mL}$ 

#### **II. Solution Route:**

T  $(Mn_2P_2O_7) = m_{crucible with precipitate} - m_{crucible}$ While, 284 g  $Mn_2P_2O_7$  is formed by 2x55 g  $Mn^{2+}$  (Mn: 55 g/mol) T g  $Mn_2P_2O_7$  is formed A g  $Mn^{2+}$  (Mn: 25 g/mol) A =  $\frac{110}{284}$  x T g  $Mn^{2+}$ While, 25 mL of sample contain A x 10<sup>3</sup> mg Mn<sup>2+</sup> 100 mL of sample contain ? mg Mn<sup>2+</sup>

The result is found as mg/100 mL.