

## 1- Inorganic reagents:

The common way to convert a particle that has no absorption(nonabsorbing species) into a particle has absorption(absorbing species) are the complexes formation reactions . The choose of a suitable chelating agent is possible to obtain a high molar absorption coefficient and therefore the ligands in the spectrometer can usually be used to estimate the precise amounts of metal ions. Table 4 shows a number of complexes formation reagents for the analysis of metal ions with spectrophotometry. The requirements for the success of spectrophotometry analysis using complexes formation reagents are :

- 1- The complexes formation reaction must be complete and equivalent.
- 2- The complex must be stable.
- 3- The complex must have absorption at the ultraviolet area or visible area.
- 4- The complex absorption spectra should not interfere with the ligand- metal ion absorption spectrum .

Additional advantages can be obtained by convert the metal ion into a complex , for example:

**First:** the reagent reacts only with a few metallic ions and therefore the reaction is selective.

**Second:** even when a number of metal ions are formed with the same reagents, the absorption properties of these complexes can be sufficiently different to allow one ion to be estimated by the presence of other metal ions.

The absorption of complex solutions is influenced by several factors, perhaps the most important of which is the effect of equilibrium. This can be illustrated by the following example: ferric ( $\text{Fe}^{3+}$ ) with thiocyanate ( $\text{SCN}^-$ ) ion is soluble red complex.



The complex ion is the ion formed from one ion react with another or more ion or with neutral molecules. The complex ion formation can be illustrated by the following equations:

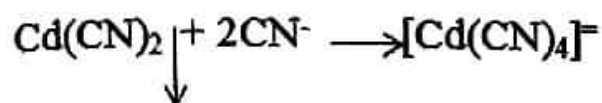


On this, the ions  $\text{ClO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{OH}^-$  are not complex ions although they are composed of more than one atom and it is appropriate to mention some of the bases that must be used to guess the formation of these complexes.

- 1- Complex ions that are often form complexes are chloride, bromide, iodide, fluoride, cyanide, thiocyanate, thiosulfide, tartarate and oxalate.
- 2- The molecules that are often form complexes are ammonia and water.
- 3- Positive ions that are not always form complexes are sodium, potassium, ammonium, magnesium, calcium, strontium and barium. An example of complex ions formation is the reaction of cadmium ion with cyanide ion when the cadmium nitrate solution is mixed with the sodium cyanide solution. In the beginning we observe a precipitate formation and then disappear when adding more cyanide ion solution to the cadmium ion solution due to the formation of the cadmium cyanide precipitate at the beginning:



When more cyanide ion is added, the precipitate begins to dissolve due to the formation of the next complex ion



From the observation of the two equations, we find that cadmium ion needs twice the amount of cyanide needed to form complex ions. A positive ion usually tends to form a series of complex ions with any reagent based on the relative concentrations of ions or reacting molecules. For example, lead ion  $[\text{PbCl}_4]^{2-}$ ,  $[\text{PbCl}_3]^-$  with chloride ion, in the presence of a high concentration of chloride ions, the second complex is formed as well as the silver ion which is  $[\text{AgCl}_3]^{2-}$ ,  $[\text{AgCl}_2]^-$ . In most analysis reactions involving the formation of complex ions, the complex agent is used with a moderate increase, therefore, it is customary to use the complex formula that is associated with a high concentration of complex reagents. Return to the Two previous examples, often used  $[\text{AgCl}_3]^{2-}$ ,  $[\text{PbCl}_4]^{2-}$ .

### **Use of inorganic reagents in analysis:**

The most important applications of inorganic reagents in analysis are:

#### **1- Masking Agents :**

It is common to use complex ions formation reagents in analytical chemistry such as masking agents. Masking agent is a substance added to the solution for the purpose of preventing certain reactions by converting the compounds involved into inactive complex compounds without separating them from the solution. For example, copper ion cannot be precipitated by hydrogen sulphide with the presence of cyanide ion as well as tin ion cannot be precipitated by hydrogen sulphide with the presence of oxalic acid.

## 2- Precipitation Reactions :

Inorganic precipitating agents are either salts of weak acids such as sulphides, carbonate, chromate and sulphate, or metal hydroxide and lead to the formation of low soluble salts or water soluble oxides with groups to be analyzed and estimated. The most important <sup>in</sup> organic precipitating agents is ammonia solution which is used for precipitation of Fe and Al ions, and hydrogen sulphide  $H_2S$  to precipitate Cu, Zn, Ge, Sn and As ions, and ammonium sulphide for precipitate of Hg and Co ions.

Complex ions can be used for the precipitation of positive and negative ions in the analysis. For example, potassium ion can be precipitate in the form of cobaltpotassium nitrite  $K_3[Co(NO_2)_6]$

Which is formed by the reaction of the cobalt ion  $Co^{2+}$  With potassium nitrite  $KNO_3$  for indirect precipitation of cobalt. Both cuppric and ferric ions can be precipitate by the ferrocyanide  $[Fe(CN)_6]^{4-}$ , potassium flosilicate ( $K_2SiF_6$ ) and sodium flosilicate ( $Na_2SiF_6$ ) are insoluble in water as well as potassium fluoroborates ( $NaBF_4$ ). Tetraphenylphenyl  $[(C_6H_5)_4 B]^-$  is excellent precipitin agent for potassium ion. In addition there are complexes (mostly chelate reagents) are insoluble in water and can therefore be used as precipitating agents such as nickel precipitation with daimethylglyoxime.

### Disadvantages:

Non-specialized, precipitate more than ion where the inorganic precipitating agent precipitate at the same time number of metal ions, causing interference when analysis ion in presence other ions. Table 4 shows some inorganic precipitating agents for cations

Weight form	Precipitate	Precipitating agent	Ions
BaCrO <sub>4</sub>	BaCrO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> CrO <sub>4</sub>	Ba <sup>+2</sup>
PbSO <sub>4</sub>	PbSO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub>	Pb <sup>+2</sup>
AgCl	AgCl	HCl	Ag <sup>+</sup>
Hg <sub>2</sub> Cl <sub>2</sub>	Hg <sub>2</sub> Cl <sub>2</sub>	HCl	Hg <sub>2</sub> <sup>+2</sup>
HgS	HgS	H <sub>2</sub> S	Hg <sup>+2</sup>
Al <sub>2</sub> O <sub>3</sub>	Al(OH) <sub>3</sub>	NH <sub>3</sub>	Al <sup>+3</sup>
BeO	Be(OH) <sub>2</sub>	NH <sub>3</sub>	Be <sup>+2</sup>
Be <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	NH <sub>4</sub> BePO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	Be <sup>+2</sup>
Fe <sub>2</sub> O <sub>3</sub>	Fe(OH) <sub>3</sub>	NH <sub>3</sub>	Fe <sup>+3</sup>
CaCO <sub>3</sub> or CaO	CaC <sub>2</sub> O <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Ca <sup>+2</sup>
Sb <sub>2</sub> S <sub>3</sub>	Sb <sub>2</sub> S <sub>3</sub>	H <sub>2</sub> S	Sb <sup>+3</sup>
As <sub>2</sub> S <sub>3</sub>	As <sub>2</sub> S <sub>3</sub>	H <sub>2</sub> S	As <sup>+3</sup>
SrSO <sub>4</sub>	SrSO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub>	Sr <sup>+2</sup>
Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	NH <sub>4</sub> MgPO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	Mg <sup>+2</sup>
Zn <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	NH <sub>4</sub> ZnPO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	Zn <sup>+2</sup>

**Table5 : some inorganic precipitating agents for anions.**

Weight form	Precipitate	Precipitating agent	Ions
AgCN	AgCN	AgNO <sub>3</sub>	CN <sup>-1</sup>
AgI	AgI	AgNO <sub>3</sub>	I <sup>-1</sup>
AgBr	AgBr	AgNO <sub>3</sub>	Br <sup>-1</sup>
AgCl	AgCl	AgNO <sub>3</sub>	Cl <sup>-1</sup>

AgCl	AgCl	FeSO <sub>4</sub> ass. ag./AgNO <sub>3</sub>	ClO <sub>3</sub> <sup>-1</sup>
CuSCN	CuSCN	SO <sub>2</sub> ass.ag. /CuSO <sub>4</sub>	SCN <sup>-1</sup>
BaSO <sub>4</sub>	BaSO <sub>4</sub>	BaCl <sub>2</sub>	SO <sub>4</sub> <sup>-2</sup>

### **The differences between organic precipitating agents and Inorganic precipitating agents:**

- 1- Co-precipitation is less if organic precipitating agents are used.
- 2- The compounds formed by organic precipitating agents are often low soluble in water and thus did not lose some of the precipitate during the process of precipitation and washing.
- 3- The compounds formed with organic precipitating are usually of very large molecular weight and thus the gravimetric factor is too small. Therefore, the percentage of elements to be estimated in the formed precipitate is low compared to inorganic compounds.
- 4- Organic precipitating agents give highly colored products, which are easy to detect by colorimetric analysis.

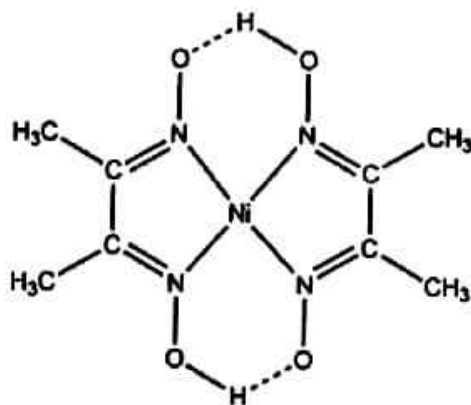
### **3- Color Formation Reactions :**

Some complexes appear in dark colors and can be inferred from their composition to detect one or both of the reagents. Thus, both the ferric ion and the thiocyanate ion can be detected from being dark red for complex  $[\text{Fe}(\text{SCN})_6]^{3-}$  and  $[\text{Fe}(\text{SCN})]^{2+}$ . Copper as a blue ammonia complex  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ .



#### 4- Chelating Complexes :

Some compounds especially organic possess chemical structure can form bonds with the central atom of any element atom in more than two positions , creating resembles cyclic structure this type of compounds called chelating compounds because the complex molecule surrounded the central ion as chelate .For example the reaction between nickel with dimethylglyoxime. The formula of  $\text{Ni}(\text{DMG})_2$  complex is :



Nickel Dimethyl Glyoxime complex

Some chelate organic compounds are very important because of their ability to form dark colored compounds and compounds that are insoluble in water. Among the most important types of complex in the analysis are:

Ammonia complexes, cyanide complexes, thiocyanide complexes, halide complexes, sulphide complexes, oxysulphide complexes, hydration complexes, hydroxide complexes, nitrite complexes, oxalate complexes.