University of Basrah
Colledge of Science
Chemistry Department

Chemical Reagents
In
Analytical and Inorganic Chemistry

By

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Chemical Reagent:

Is a "substance or compound added to the system for chemical reaction or added to observe the reaction occurance" . Although reactant and reagent terms are often used interchangeably, the reactant is less specific "substance consumed in the context of chemical reaction". Although solvents and catalysts include in the reaction, they usually do not referred to as reactants.

In organic chemistry, reagents are compounds or mixtures, usually composed of inorganic molecules or small organic molecules, which are used to influence the transformation of the organic substrate.

Examples of organic reagents include : Collins reagent , Fenton reagent , and Grignard reagent . There are also analytical reagents that are used to confirm the presence of another substance. Examples of these reagents are Fehling reagent, Millon reagent and Tollens reagent . In another use of this term, when purchasing or preparing chemicals, the quality of the reagent shows that the chemicals are sufficiently pure to be used in chemical analysis, chemical reactions or physical testing. Standards for purity of reagents have been developed through organizations such as the American Society for Testing International Materials (ASTM). For example, the quality of a chemical reagents must possess very low levels of impurities such as sodium ions, chloride, silica , and bacteria, in addition to their very high electrical resistance.

* **The most important chemical reagents** :

Lime water, bromine water, iodine solution, alcohol iodine solution , Fehling′s solution, starch solution, Phenolphthalene , methyl orange , methyl red .

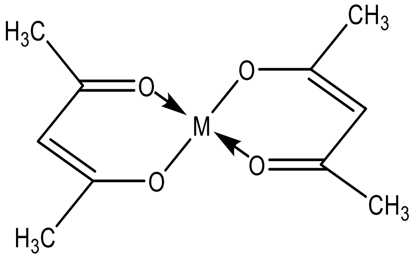
Chemical reagents are divided into Two types:

1- Organic reagents
2- Inorganic reagents

1- Organic reagents :

Many chemical reagents, especially organic reagents, are of great importance in many areas of chemistry, such as analytical chemistry , inorganic chemistry , and medical biological chemistry .

These reagents have the ability to coordinate with many metals because it contain acidic or basic groups with unpairs electrons on oxygen, nitrogen or sulfur are available for donation to form complexes . In addition, the location of the acidic or basic groups in the organic reagent should be suitable for the formation of a ring containing metal and relatively tension free. As in the complex resulting from the reaction of metals with beta di ketone :



Metal β -diketone

These reagents have spread widely and have many applications and uses for the following advantages:

1- High Molecular Weights: This property allows it to obtain a relatively large precipitate the small amount of metal ions, which allows it to be important reagents in precise quantitative analysis.

2- It is highly selective where the precipitation and separation of metal ion can be carried out without a specific reagent.

3- The distinctive colors of their complexes: this makes them suitable in qualitative and chromatic analysis and in the spots tests.

4- Co-precipitation: the precipitates that produce by these reagents with metals are of a non-ionic covalent nature so that they are not contaminated with ionic impurities, ie they are free from co-precipitation.

5- Solubility of its complexes in organic solvents: therefore, used in solvent extraction processes.

Despite the previous advantages of organic reagents, they have some of the following disadvantages:

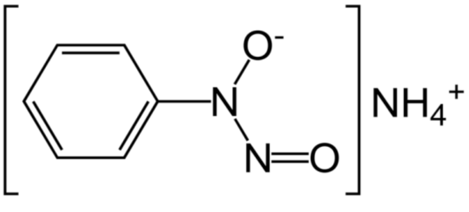
1- Highly volatile where it is affected by heat because the weak bonds between their molecules.

2- Its compounds are non- polar : they are insoluble in water, making us not use polar solvents like water to prepare their solutions.

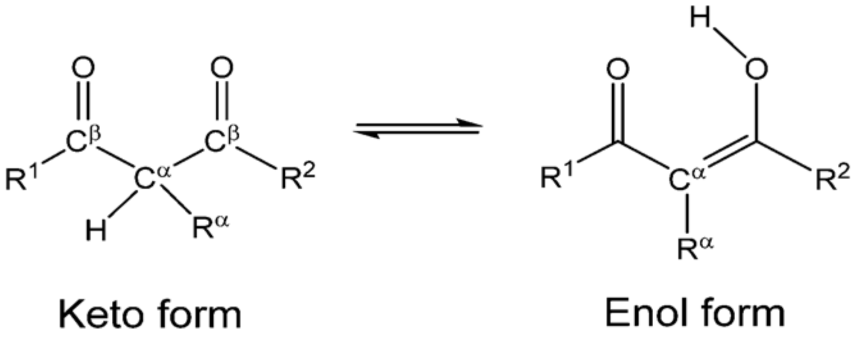
3- Its low purity : cannot be prepared with high purity, some of which have isomers in preparation.

In analytical chemistry, it is capable of forming coordination complexes with distinct colors, and its importance in this field is its high selectivity and sensitivity, for example the use of Dimethyl glyoxime to detect nickel.

Organic reagents are general when oxygen is the unique donor in the molecule as in β - diketone and Cupferron .

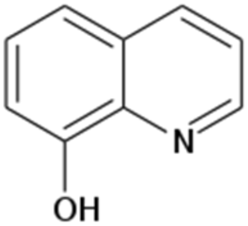


Ammonium - *N*- nitrosophenylhydroxylamine (Cupferron)



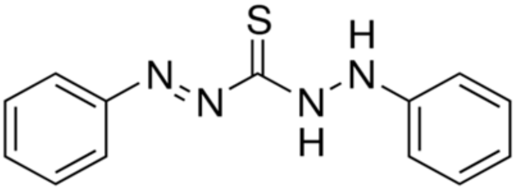
β - diketone

The selectivity are increase when the organic reagent contains a nitrogen atom as well as oxygen as in: 8-Hydroxy quinoline

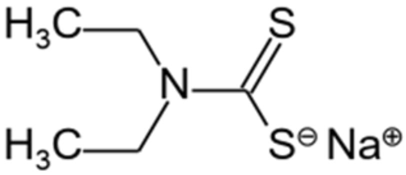


8-Hydroxy quinolone

On the other hand, organic reagents containing nitrogen and sulfur such as Dithizone and Diethyldithiocarbamate are Highly selective for metallic elements Bi $^{2+}$, Cu $^{2+}$, Ag $^{2+}$, Hg $^{2+}$, Zn $^{2+}$, Cd $^{2+}$, Pb $^{2+}$ As^{2+} well as noble transition metals.

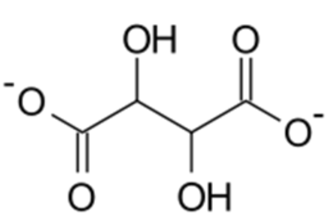


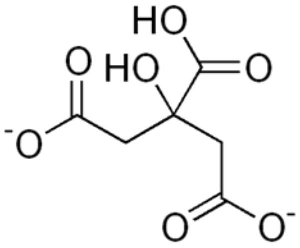
Dithizone

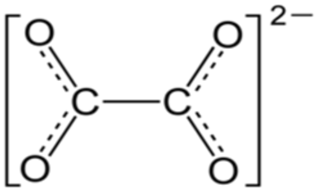


Sodium Diethyl dithiocarbamate

Reagents, which contain oxygen such as oxalates, tartarates and citrares which are not charged chelates, are considered masking agents of ions .

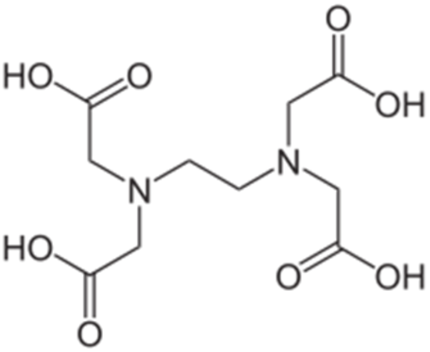






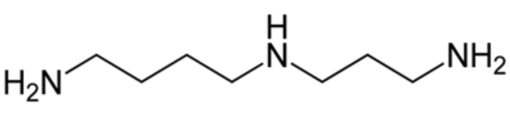
Tartarate **Citrate** **Oxalate**

As well as Amines polycarboxylic acids reagents such as Ethylene diamine tetraacetic acid (EDTA) are general masking agents due to the large number of oxygen atoms in the molecule relative to the number of nitrogen atoms.

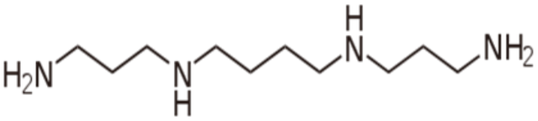


Ethylendiaminatetraacetic acid (EDTA)

On this basis the polyamines reagents such as Spermidine and Spermine are more selective and coordinate only with the bivalent metals of B group and transition metals. While it is difficult to have a affinity to the positive ions of A group .

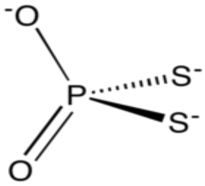


Spermine

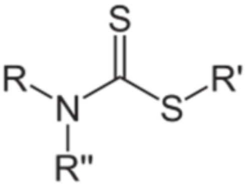


Spermidine

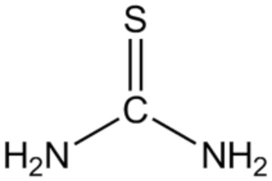
Sulfur is still more selective in the organic reagents such as Thio urea , Diethocarbamate and Diaphosphate Dithiophosphate .



Dithiophosphate



Dithiocarbamate

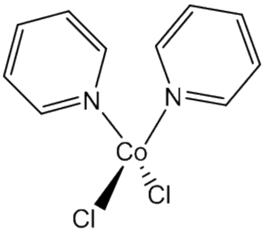


Thiourea

Classification of organic reagents:

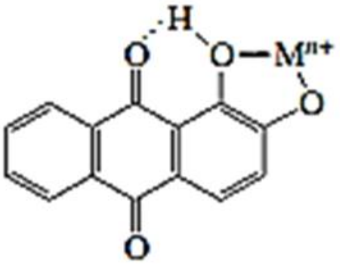
Organic reagents can be classified according to the bonding groups to :

1- Monodentate reagents : It contains a monobonding group such as pyridine.



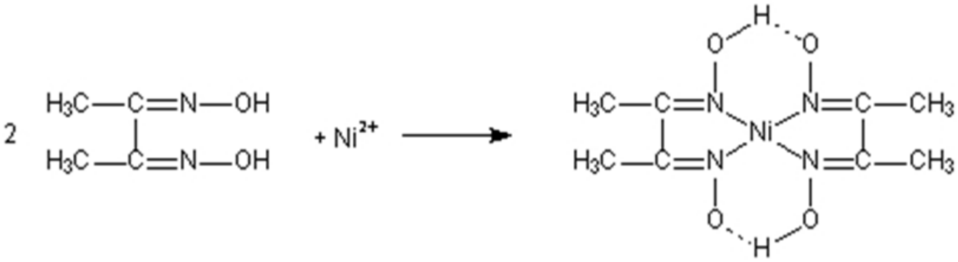
Cobalt Pyridine

2- Bidentate Reagents : The reagent molecules are bibonding pentagonal or hexagonal ring that is strainless ring with metal ions such as 8-Hydroxy quinolone , Dimethylglyoxime and Alizarin . The chelate ring formed with the alizarin with metals is by oxygen in the hydroxyl group at the first and second sites, respectively.



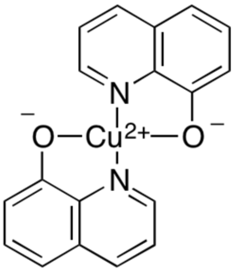
Metal Alizarin

In the case of Dimethylglyoxime, the metal ion forms a bond with the nitrogen atoms in DMG . The reaction with nickel ion is as follows:



Dimethylglyoxime **Nickel Dimethylglyoxime**

In case 8-Hydroxy quinoline ,the metal ion forms a bonds with both phenol oxygen (immediately replacing the hydrogen) and the ring nitrogen. The reaction with the copper ion is as follows:

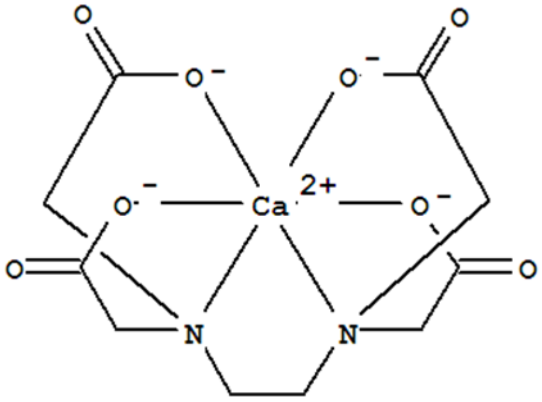


Cupper - 8-Hydroxy quinoline

3- Polydentate Reagents :

These reagents can have a larger number of the chelate rings, such as Tridentate reagents and Tetradentate reagents and Hexadentate reagents .These reagents have more than two groups of bonding within a single molecule found in positions that can form more than chelate ring with one metal ion. As an example:

Ethylene Diamine Tetra Acetic Acid (EDTA) Which can occupy four or six locations. In other words, they can form hexadentate, but they often react as tetradentate with matals through Two nitrogen atoms and one of the carboxylic groups in both nitrogen atoms as in their reaction with calcium:



Calcium - Ethylene Diamine Tetra Acetic Acid (EDTA)

Functional classification of organic reagents :

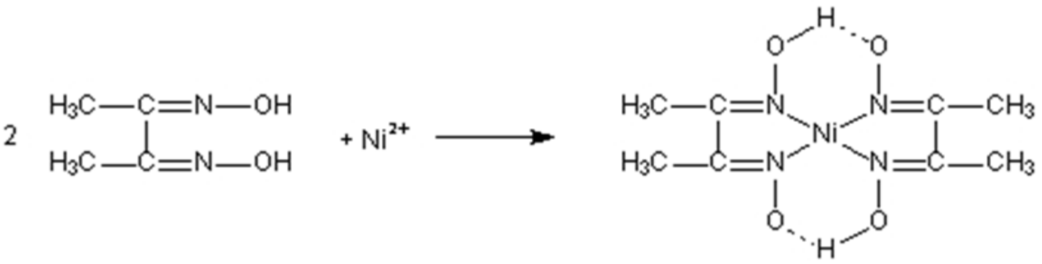
Under certain conditions, some organic reagents react with a group of cations or metal ions, and so are reagents called selective reagents . If the reaction occurs with only one metal ion, the reagent is called specific reagent .

The specific properties of the reagents are often limited to only a certain experimental conditions . It is possible to conclude that the selective properties of organic reagents are due to the presence of special groups in the molecules called the functional groups in the analytical functional classification .

The following are some of the most important groups in the analysis :

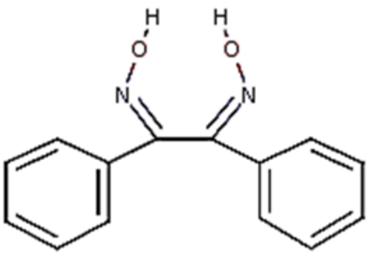
1- Dioximes :

The oximeimino group are present in the specific reagent for nickel such as Dimethylglyoxime and as shown :

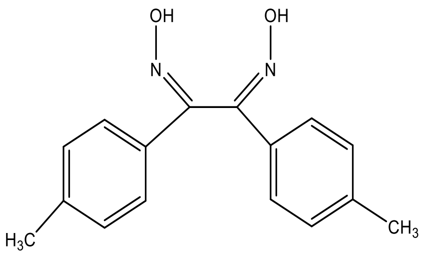


Nickel Dimethylglyoxime **Dimethylglyoxime**

Several reagents prepared but the reactivity toward nickel has remained constant as an example Benzyldioxime and Methyl benzyldioxime :



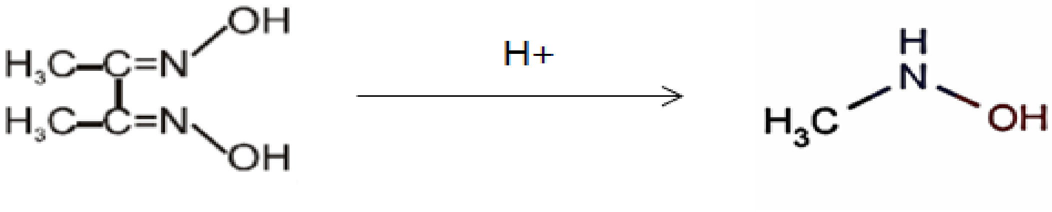
Benzyldioxime



Methyl benzyldioxime

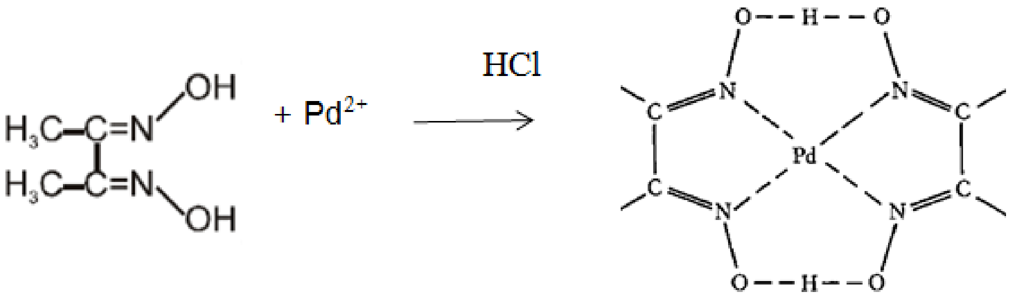
Many other reagents in this family are used but DMG is remained the most used which is defined firstly by Chugaeff since 1905 .

Dimethylglyoxime is a specific reagent for nickel in a weak ammonia medium where nickel is precipitate as a red crystal precipitate which used in both quantitative and qualitative analysis of nickel. The nitrogen atoms are distributed around the metal in a square planer and the hydrogen atoms are form hydrogen bridge between oxygen atoms. Dimethylglyoxime in the acidic medium transport to hydroxylamine which can then be estimated by oxidation titration:



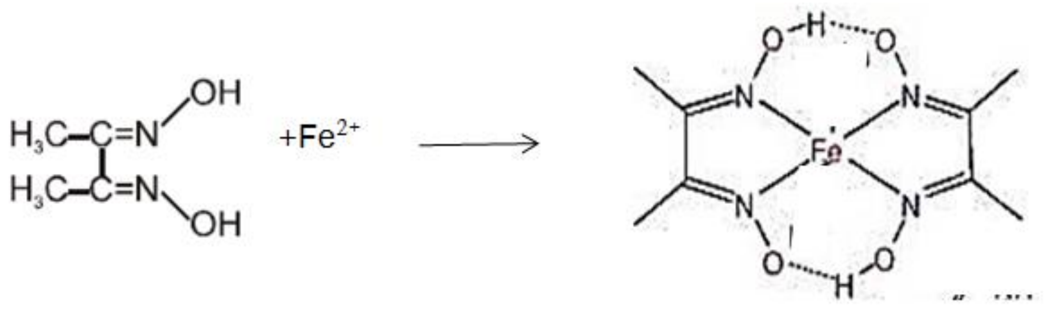
DMG **hydroxylamine**

Dimethylglyoxime can be also used to detect palladium, which is a yellowish precipitate in a slightly acidic medium with hydrochloric acid:



Dimethylglyoxime Palladium Dimethylglyoxime

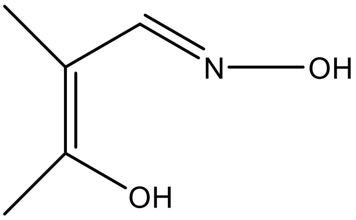
Another sensitive reaction of this reagent is the formation of a dark red solution with ferrous ions different of the crystalline precipitate of the nickel complex. The composition of the dissolved red complex with iron ions is Fe (DMG) $_2$ .2NH $_3$ and the reaction is as follow:



Dimethylglyoxime FerrousDimethylglyoxime

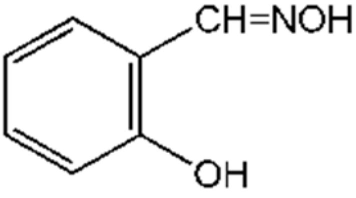
2- HydroxyOxime :

When the general form is included within the organic system :



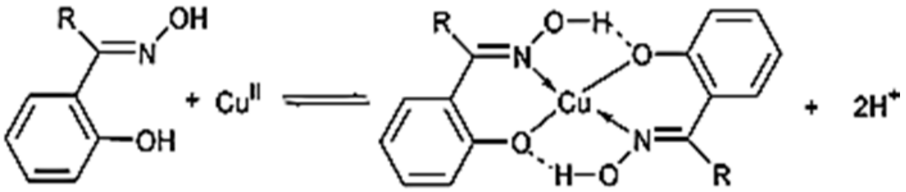
HydroxyOxime

It is form chelate compound with certain metals such as Pd $^{2+}$, Ni $^{2+}$, Pb $^{2+}$, Hg $^{2+}$ …etc. , and most specific with copper and the best medium of precipitation is weak acidic. The ideal reagent in is Salicylaldoxime



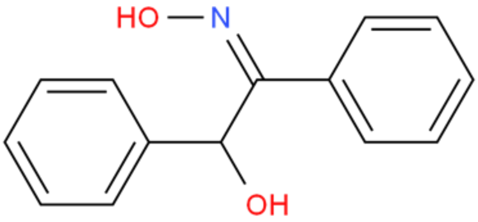
Salicylaldoxime

Which is considered as the best precipitating agent to copper and the general structure of the chelate compound is as follows:



3- Acyloin Oxime :

Are specific reagent for copper in the ammonia medium where produce amorphous green precipitate and the most important reagents in this group is α-Benzoin Oxime which is in some cases called Cupron

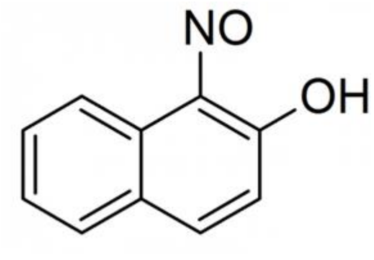


α-Benzoin Oxime (Cupron)

The existence of some mineral salts which is precipitate in ammonia medium ,the precipitation of this mineral salts in the ammonia solution can be prevented by adding sodium or potassium tartarates.

4- Ortho-Nitrosophenols :

Are selective reagents of cobalt salts and the typical reagent of this type is α-Nitriso-β-Naphthol which is proposed by Hyinskiy in 1885 as the first organic reagent in the inorganic analysis .

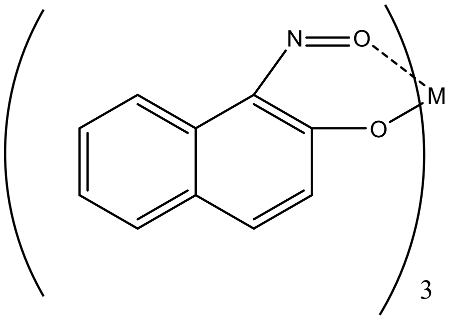


α-Nitriso-β-Naphthol

The precipitate complex with cobalt is formed only in a weak basic or neutral medium, but if the formed precipitate does not dissolve in dilute mineral acids.

While in the acidic medium the precipitation does not occur and as a typical internal compound salts it dissolves with non-polar solvents such as chloroform and carbon tetrachloride. Similar reactions occur with ions Fe $^{2+}$, UO $_2$ $^{2+}$, Cu $^{2+}$ and Hg $^{2+}$.

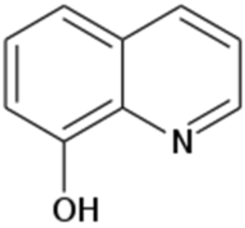
The greatest importance of the α-Nitriso-β-Naphthol reagent is the probability of cobalt detection and estimation , although in the presence of nickel salts. The precipitate complex structure is not well defined, so it should be burned to oxides and weighed in this formula:



Metal - α-Nitriso-β-Naphtho

5- 8-Hydroxy quinolone (Oxine) :

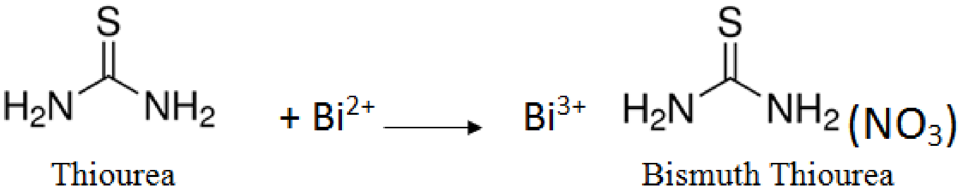
This reagent generally possesses a group that leads to the formation of a pentagonal ring. Oxine reagent is widely used and has been used to detect and estimate approximately thirty elements. The selectivity of this reagent can be increased by controlling the pH of the solution using an additional masking agent. Most of the formed chelate compounds are in the form of crystalline precipitates and are sufficiently pure to be dried and weighed in this form. The weight can be replaced by titrations process using bromate,



8-Hydroxy quinoline

6- Thio carbonyl group C = S :

Is a functional selective analytical group of bismuth Bi^{2+}. The simplest and first reagent in this group is Thiourea which gives a yellow-colored solution with bismuth in an medium of diluted nitric acid . This reaction is a qualitative test of the (IIA) group and all other elements . Only antimony gives a pale yellow color and yellow color of the thiourea complex with bismuth is illustrated by the following reaction:

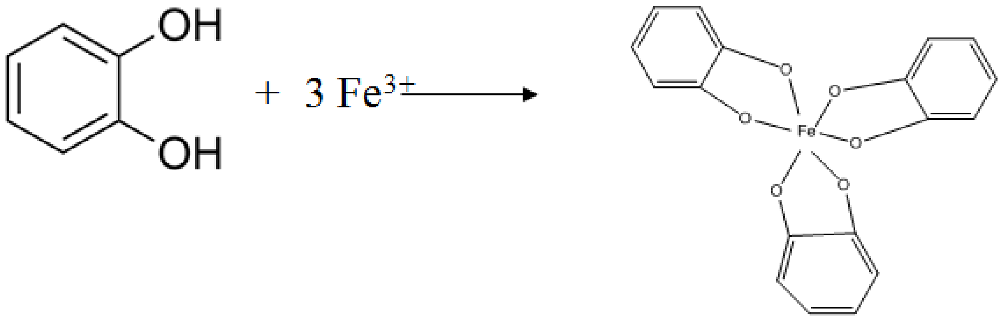


7- Phenols Phenols :

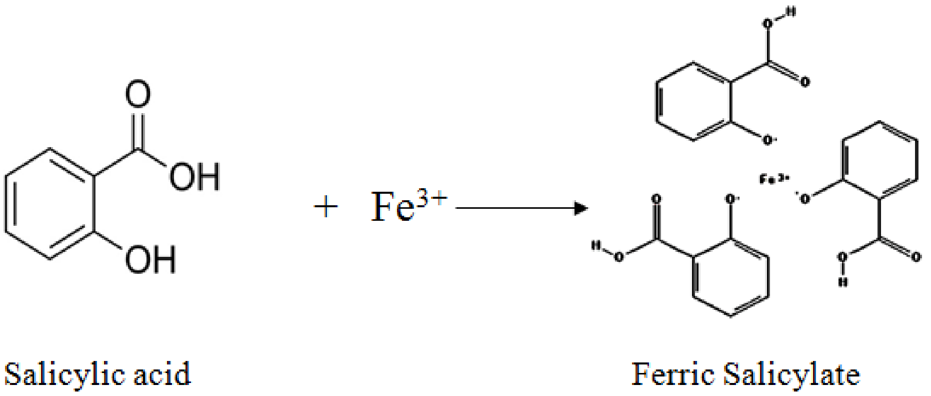
It gives a series of specific color reactions applied in some of analytical purposes and reaction involving either complex formation or oxidation reaction reaction .

The phenolic groups are analytical functional groups of Iron and the presence of another oxygen-containing group at the Ortho site increases the complex stability and increases the coloring ability . The color of the complex depends on the phenolic concentration and pH of the solution, the distinctive chromatic reactions represented by Pyrocatechine and the resulting color depends on the pH range of the solution where the light blue in the acidic medium ranging between (PH = 3-1) and a purple at acidic medium ranging between (pH = 5-3) and dark red in the basic medium .

The complex resulting by the reaction between Pyrocatechine and ferric is as follows :

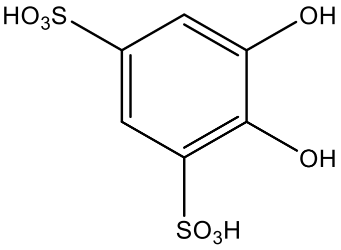


Another analytical reagent for ferric is salicylic acid which is gives the following colors:



The color is reddish purple when the solution is more acidic than pH = 3 and red when pH = 3-5 and yellowish orange in a basic medium.

Salicylic acid produce a series of complexes: [FeR], [FeR $_2$], [FeR $_3$] ^{3} Where R is salicylic acid. While pyrocatechine-3,5-disulphonic acid was suggested as metal indicator.



Pyrocatechine-3,5-disulphonic

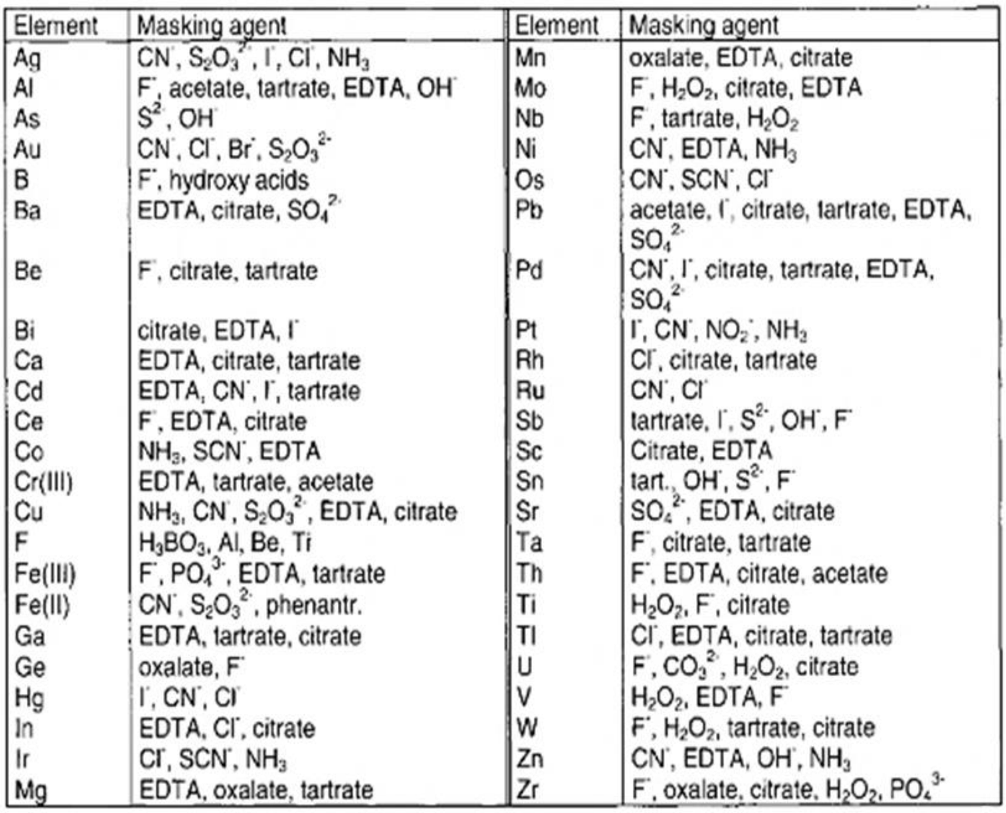
The most important applications of organic reagents in analysis:

The largest part of the organic reagents used in analytical reactions react to the formation of chelate and there is a small group of organic reagents are form ionic compounds with metals and some dyes are used for the precipitate coloration. Organic reagents are also used in oxidation - reduction reactions.

1- Masking Agents :

The masking agent is a substance added to the solution for the purpose of preventing certain reactions by converting the compounds involved into non-effective complex compounds without separation them physically from the solution. The use of complex ions formation reagents in analytical chemistry as masking agents is known. Table 1 shows some of compounds that are used as masking agent for some certain elements:

Table1: Some of compounds that are used as masking agent for some certain elements.



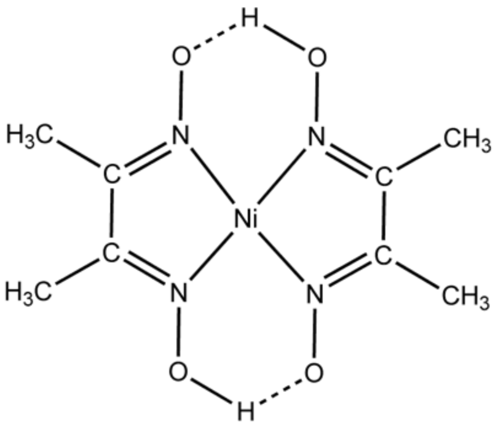
Element	Masking agent	Element	Masking agent
Ag	CN^-, $S_2O_3^{2-}$, I^-, Cl^-, NH_3	Mn	oxalate, EDTA, citrate
Al	F^-, acetate, tartrate, EDTA, OH^-	Mo	F^-, H_2O_2, citrate, EDTA
As	S^{2-}, OH^-	Nb	F^-, tartrate, H_2O_2
Au	CN^-, Cl^-, Br^-, $S_2O_3^{2-}$	Ni	CN^-, EDTA, NH_3
B	F^-, hydroxy acids	Os	CN^-, SCN^-, Cl^-
Ba	EDTA, citrate, SO_4^{2-}	Pb	acetate, I^-, citrate, tartrate, EDTA, SO_4^{2-}
Be	F^-, citrate, tartrate	Pd	CN^-, I^-, citrate, tartrate, EDTA, SO_4^{2-}
Bi	citrate, EDTA, I^-	Pt	I^-, CN^-, NO_2^-, NH_3
Ca	EDTA, citrate, tartrate	Rh	Cl^-, citrate, tartrate
Cd	EDTA, CN^-, I^-, tartrate	Ru	CN^-, Cl^-
Ce	F^-, EDTA, citrate	Sb	tartrate, I^-, S^{2-}, OH^-, F^-
Co	NH_3, SCN^-, EDTA	Sc	Citrate, EDTA
Cr(III)	EDTA, tartrate, acetate	Sn	tart., OH^-, S^{2-}, F^-
Cu	NH_3, CN^-, $S_2O_3^{2-}$, EDTA, citrate	Sr	SO_4^{2-}, EDTA, citrate
F	H_3BO_3, Al, Be, Ti	Ta	F^-, citrate, tartrate
Fe(III)	F^-, PO_4^{3-}, EDTA, tartrate	Th	F^-, EDTA, citrate, acetate
Fe(II)	CN^-, $S_2O_3^{2-}$, phenantr.	Ti	H_2O_2, F^-, citrate
Ga	EDTA, tartrate, citrate	Tl	Cl^-, EDTA, citrate, tartrate
Ge	oxalate, F^-	U	F^-, CO_3^{2-}, H_2O_2, citrate
Hg	I^-, CN^-, Cl^-	V	H_2O_2, EDTA, F^-
In	EDTA, Cl^-, citrate	W	F^-, H_2O_2, tartrate, citrate
Ir	Cl^-, SCN^-, NH_3	Zn	CN^-, EDTA, OH^-, NH_3
Mg	EDTA, oxalate, tartrate	Zr	F^-, oxalate, citrate, H_2O_2, PO_4^{3-}

2 - Precipitation Reactions :

It include the addition of material to another material solution to precipite it and there are some qualities must be provide in the precipitating agent which**:**

1- Be specific so as not to cause interference.
2- To give a precipitate with a large molecular weight.
3- The precipitate must be low solubility.
4- To gives a very bright color product.
5- The resulting precipitate crystals are large enough to be easily washed and filtered.
6- To be a high purity.

The Organic precipitating agents are organic compounds used to precipitate some metallic ions where some cyclic compounds are chelate complex with very low solubility such as dimethylglyoxime which is used to precipitate nickel in alkaline medium and with palladium in the acidic medium , $Ni(DMG)_2$ chelate structure contains covalent ~~bon~~d representing ( ) and coordination bonds (-----). These bonds bind two molecules of DMG with nickel.

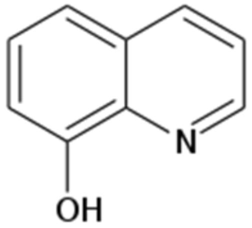


Nickel Dimethyl Glyoxime complex

This chelate compound is stable because it contains two pentagonal rings and two hexagonal rings. In addition, this organic reagent can form chelate compounds with zinc, copper and cobalt. These compounds are dissolved in water. Therefore, these metals can not be estimated by the quantitative gravimetric methods by using this reagent.

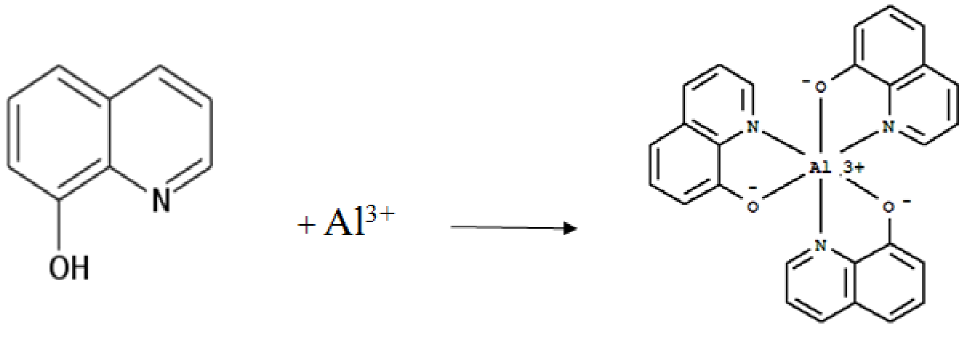
- 8-Hydroxyquinoline(Oxine)

This reagent has the ability to precipitate some of metal ions depend on the pH value.



8-Hydroxyquinoline(Oxine)

This reagent can form chelate compound with aluminum and magnesium both individually and under controlling conditions , for example, its reaction with aluminum is as follows:



8-Hydroxyquinoline

Al^{3+} 8-Hydroxyquinoline

There is a type of reagents called metal organic reagent, which consists of organic part usually aliphatic rings or aromatic rings and inorganic part represented by element and this reagents behave as ions because it contain a negative charge reacts strongly with the positive ions to be estimated, produce low solubility precipitates similar to salts such as Tetraphenylsodiumborate BNa $(C_6H_5)_4$ Which is highly selective in potassium precipitation . Also TetraphenylarsoniumChloride $[(C_6H_5)_4As]^+$ Cl Where it gives the positive Tetraphenylarsoniumthat in water and react with the negative ion of mercury as follows:

$2\ (C_6H_5)_4\ As^+ + HgCl_4^{-2} \rightarrow [(C_6H_5)_4As]_2\ HgCl_4$

Advantages of the precipitation using organic reagents:

1- Organic reagents (organic precipitants) are selective or can be selective by using a optimum pH or controlled by masking method.

2- Precipitates are easily dried at temperatures below 100 °C.

3-The formed precipitates are mostly non-ionic and do not absorb impurities strongly.

4- The formed precipitates are soluble in organic solvents.

Disadvantages of organic reagents (organic precipitants):

1- Organic reagents are viscous always and difficult to transfer from beaker to another.

2- Organic reagents are not very pure.

2- Organic reagents rarely soluble in water and the small increase of the the precipitating agent causes precipitate contamination. Table2 shows some organic precipitating agents.

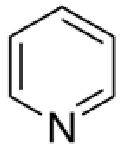
Table2 : some organic precipitating agents.

Element	**Precipitating agent**	**Precipitation formula**	**Weight formula**
Ni^{+2}	Dimethyl glyoxime (DMG)	$Ni(C_4H_7O_2N_2)_2$	$Ni(C_4H_7O_2N_2)_2$
Fe^{+3}	Cupferon	$Fe(C_6H_5N_2O_2)_3$	Fe_2O_3
Cu^{+2}	Neocupferon	$Cu(C_{14}H_{11}O_2N)$	$Cu(C_{14}H_{11}O_2N)$
Co^{+2}	α-Nitroso-β-naphthol	$Co(C_{10}H_6O_2N_3)$	$CoSO_4$
K^+	Sodium tetra phenyl boron (NaTPB)	$K[B(C_6H_5)]_4$	$K[B(C_6H_5)]_4$
Ca &Mg	Oxalic acid	MgC_2O_4 , CaC_2O_4	MgC_2O_4 , CaC_2O_4
Hg	Chloride Phenyl Arsenic $[(C_6H_5)_4As]^+Cl$	$[(C_6H_5)_4As]_2HgCl_4$	$[(C_6H_5)_4As]_2HgCl_4$

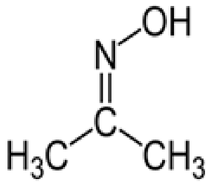
4- **Chelating Complexes** :

The organic reagent molecule can be bonded with metal ion through the O, N, S atoms as in :

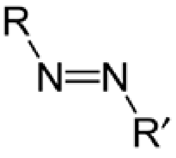
- Some oxygen containing groups such as -OH, -CO, -COOH, -CHO
- Some nitrogen containing groups such as $-NH_2$, = NH ,and aromatic nitrogen as in pyridine and nitrogen in oxime and Azo groups.



Pyridine

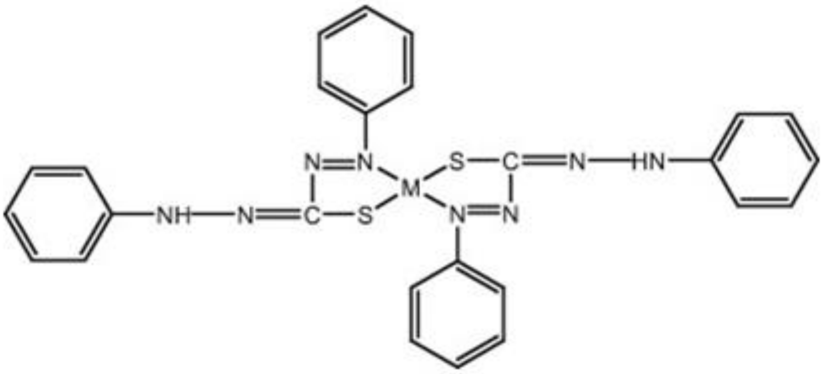


Oxime



Azo

- The aliphatic sulfur, as in dithizone is the only one that can react with metals because the heterogeneous cyclic sulfur does not have enough electron donation force for bonding.



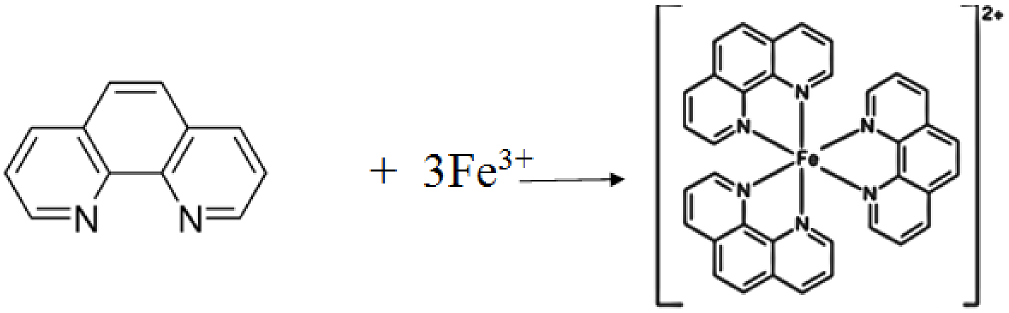
Metal Dithizone

4- Color Formation Reactions :

The absorption spectra of the chalet compounds is due to the electronic oscillations occurring within the metal ion within the reagent molecule and between metal and chelates. A large number of the formed chelate May be concerned with important changes in the visible region of the spectrum and then the coloring of the solutions. This phenomenon can be used in many cases in color measurement analysis and can be explained by several examples of applications of organic reagents, including:

1- Orthophenanthroline:

This reagent is called 1,10-Phenanthroline, which is a very sensitive reagent to detect and measure the color of iron and gives a dark red color with ferrous , the resulting complex is as follows:

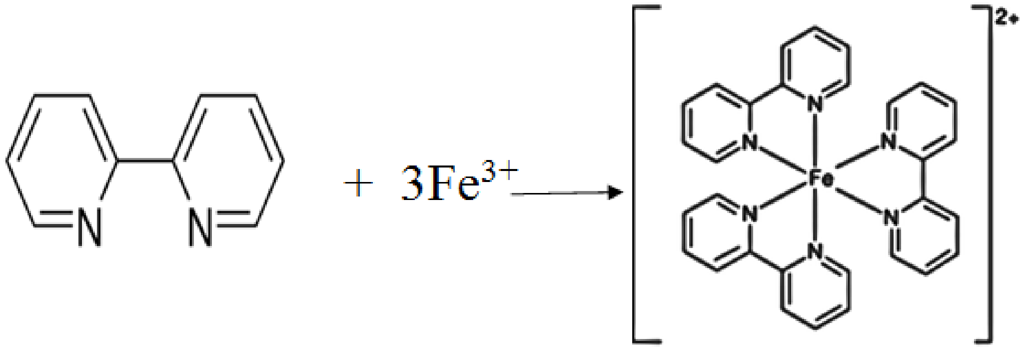


1,10-Phenanthroline Iron 1,10-Phenanthroline

Iron(1,10-Phenanthroline)$_3$ is stable in the acidic medium and is suitable for trace color measurements of iron and to estimate iron in wine, leather and other biological materials.

2- α-Bipyridyl:

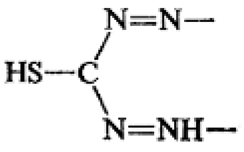
This reagent reacts with ferrous in the same way as 1,10-Phenanthroline with the same general form but not the same degree of stability and is used to detect trace amounts of iron ferrous in ferric. The red solutions of these complexes can be used as indicators in the oxidation - reduction reactions because the reaction is reverse and the system has a high oxidation-reduction voltage of 1.1 volts.



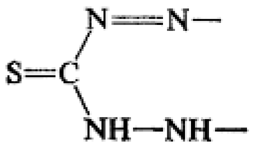
α- Bipyridyl Iron α- Bipyridyl

3- Dithizone:

This reagent is also called diphenylthiocarbazone and is found in two forms: Keto form and Enol form as shown:

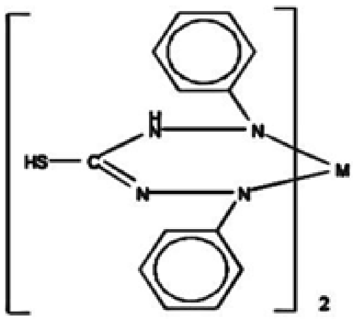


Enol form

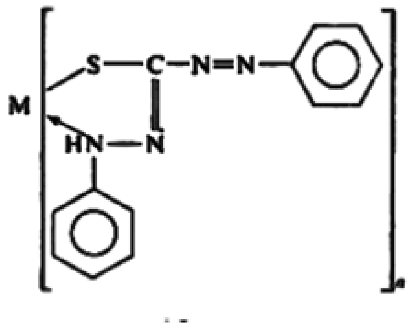


Keto form

Dithizone was originally discovered for qualitative detection of heavy metals and was used to estimate colorimetric measurements, especially in trace analysis where dark-colored chelate complexes can be formed and extracted into non-polar solvents such as CCl_4. This is a very suitable method for separating trace amounts of metals. There are Two types of complexes can be form:



Keto form complex



Enol form complex

The Enol form of dithizone complexes consist of metals that are good sulfide derivatives in basic solutions and the selectivity of dithizone can be increased by:

A) Control pH of the extracted solution:

The reliability of the extraction ability of a number of dithizone on pH of the solution can be expressed in the extraction curves, Which have typical forms in the form of (S) and each curve is distinguished by the value of pH at the middle of the extraction and this value is $pH_{1/2}$ can be attributed to the stability constant of the chelate compound:

$$pH_{1/2} = (1 / n) \log K$$

The difference in two values of pH is necessary for successful separation.

B) Addition of complex reagents to mask interfering metals ions :

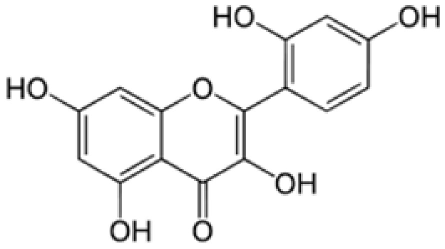
In weak alkaline solutions containing cyanide ion CN^- and tartarate, only bismuth (Bi) and lead (Pb) are extractable. If the medium contains KCNS and the solution is adjusted with sodium acetate, only mercury(Hg) alone can be extracted with gold (Au) and platinum (Pt) .

C)Oxidation - reduction of interfering metals :

As an example , platinum Pt^{2+} react with the dithizone in the same way as palladium Pd^{2+} but platinum Pt^{4+} do not react with the dithizone.

4- **Florescent Reagent:**

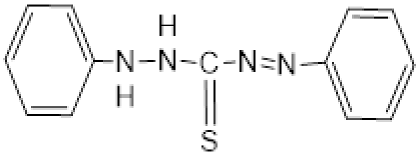
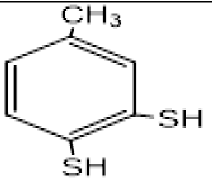
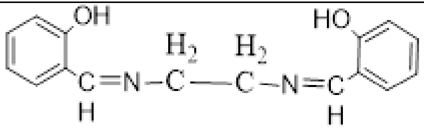
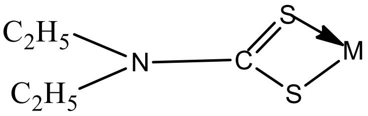
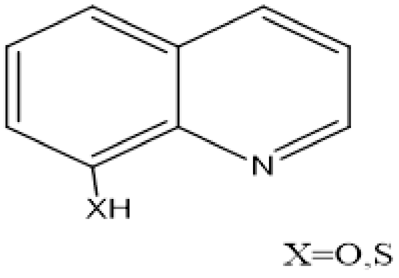
This reagent is called a Morin reagent and it has a chemical formula:

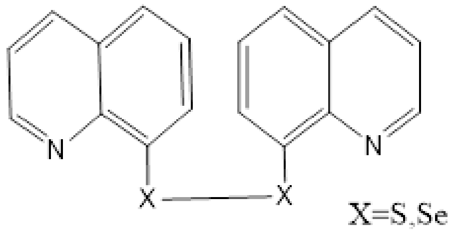
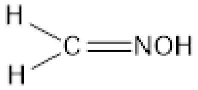
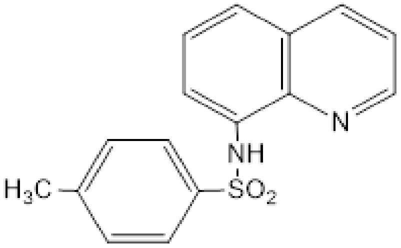
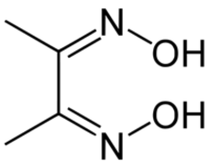
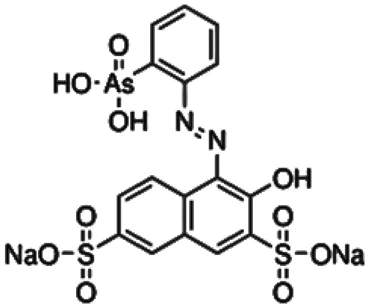
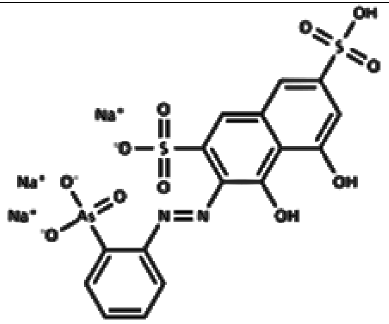


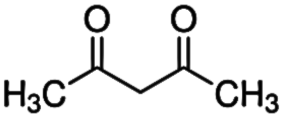
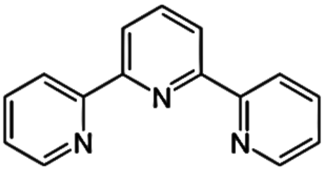
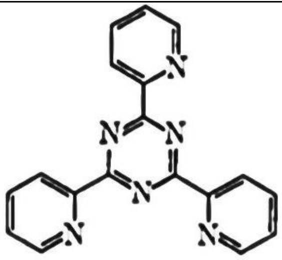
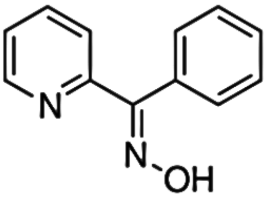
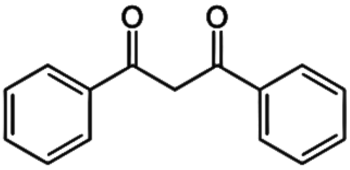
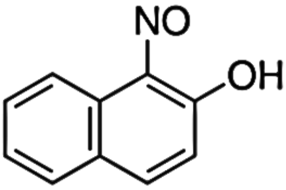
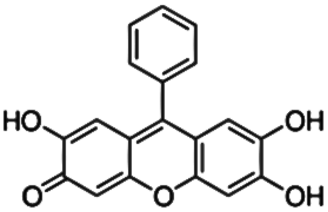
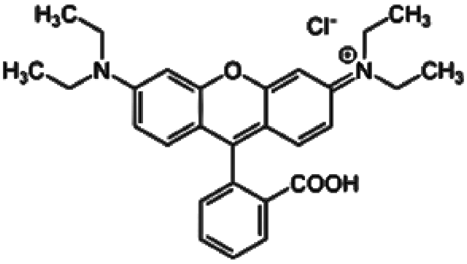
3,5,7,2,4-Pentahydroxy flavone (Morin)

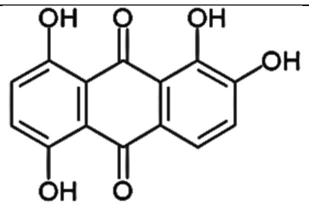
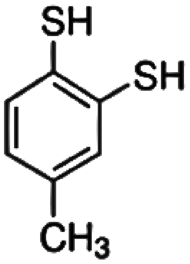
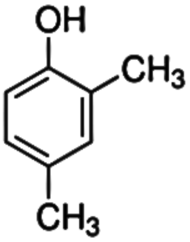
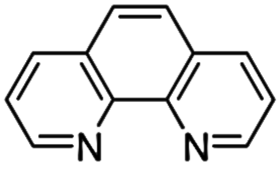
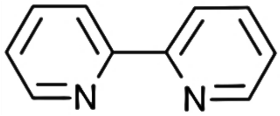
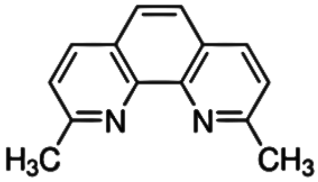
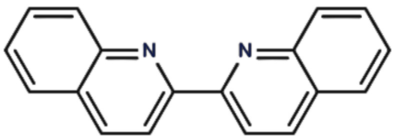
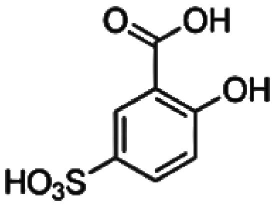
Morin reagent react with aluminum (Al^{3+}) ion to produce a dark green fluorescent color that can be used to estimate trace amounts of aluminum (Al^{3+}). Beryllium (Be), gallium (Ga), indium (In) and scandium(Sc) are coordinate with oxygen and their complexes of the same fluorinated color but these ions can be easily separated from aluminum ions .

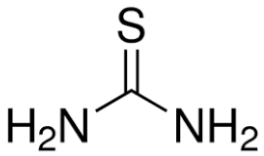
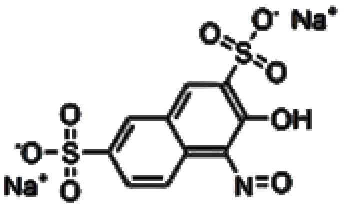
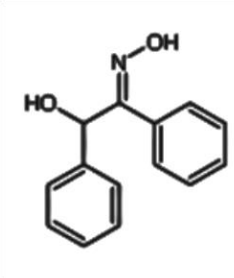
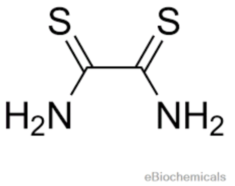
Table3: shows some organic agents.

No.	**Reagent**	**Chemical Structure**	**Determined Element**
1	Dithizone		(Pb^{2+} , Zn^{2+} ,Cd^{2+} ,Hg^{2+} ,Ag^{+} ,Cu^{2+}, Bi^{3+} , Pd^{2+} and other metals)
2	Dithiol		Sn^{2+},W^{6+},Mo^{6+}
3	Bis-salicylal ethylenediamine		Mg^{2+}
4	Sodium diethyl dithiocarbamates		(Bi, Cu, Fe, Ni, Co, Pb, Te, As, Se, and Mn)
5	8-Hydroxyquinoline (0xine) Or 8-Mercaptoquinoline (thio-oxine)		(Fe^{3+}, Cu^{2+}, Mn^{2+} , Co^{2+} ,Mo^{6+} ,V^{4+} ,Ni^{2+} ,Pd^{2+} , Os^{3+} Zn^{2+}, Al^{3+}, Ce^{3+}, Ga^{3+}, In^{3+}, Mg^{2+}, Sc^{3+} and Ru^{3+})

6	8,8´- Diquinolydisulphide Or 8,8´- Diquinolydiselenuim		Cu^{2+}
7	Formaldoxime		(Ni , Mn , Cu , Fe, V , Co , and Ce)
8	8- Tosylaminoquinoline		Zn^{2+},Cd^{2+}
9	Thiocyanate	(KSCN, NaSCN ,NH_4SCN)	.(Zn, Cd, Cu)
10	Dimethylglyoxime (DMG)		Ni(II)
11	Thoron		Th(IV) , Zr(IV)
12	Arsenazo		Hf (II) , Zr (IV)

13	Acetylacetone		Be(III)
14	2,2,2, Terpyridine		Co(II)
15	2,4,6-Tripyridyl-s-triazine		Fe(II)
16	Phenyl-2-pyridyl ketoxime		Fe(II)
17	Dibenzoylmethane		UO_2(II)
18	1-Nitroso-2-naphthol		Co(II)
19	9-Phenyl-2,3,7-trihydroxy-6-fluorone		Ge(IV)
20	Rhodamine B		Sb(V)

21	Quinalizarin		B
22	Toluene-3,4-dithiol		Sn(IV) , Mo(V) , W(VI)
23	2,4-Xylenol		NO_3^-
24	1,10-Phenanthroline		Fe(II)
25	2,2-Bipyridine		Fe(II)
26	2,9-Dimethyl-1,10-phenanthroline		Cu(II)
27	2,2-Biquinoline		Cu(II)
28	Sulfosalicylic acid		Al(III) , Ti(IV)

29	Thiourea		Bi(III) , Os
30	Nitroso R salt		Co(II)
31	Benzoin α-oxime		Cu(II) , Mo(V)
32	Dithiooxamide		Ni(II) , Co(II) , Cu(II) , Bi(III)

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 (Fe^{3+}) with thiocyanate (SCN^{-}) ion is soluble red complex.

$$Fe^{3+} + 6SCN^{-} \longrightarrow [Fe(SCN)_6]^{3-}$$

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:

$$Fe^{3+} + 6CN^- \rightleftharpoons [\,Fe(CN)_6]^{3-}$$

$$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2-}$$

$$2Cl^- + HgCl_2 \rightleftharpoons [HgCl_4]^{2-}$$

$$Cu^{2+} + 4H_2O \rightleftharpoons [Cu(H_2O)_4]^{2+}$$

$$I^- + I_2 \rightleftharpoons I^{3-}$$

On this ,the ions ClO_3^-, $CO_3^=$, $SO_4^=$, PO_4^{3-}, CH_3COO^-, 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:

$$Cd^{2+} + 2CN^- \longrightarrow Cd(CN)_2$$

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

$$Cd(CN)_2\downarrow + 2CN^- \longrightarrow [Cd(CN)_4]^=$$

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 ions 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 $[PbCl_4]^=$, $[PbCl_3]^-$ 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 $[AgCl_3]^=$, $[AgCl_2]^-$. 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 $[AgCl_3]^=$, $[PbCl_4]^=$.

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 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 ($NaBF_4$). Tetra phenylphenyl $[(C_6H_6)_4 B]^-$ is excellent precipitatin 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. Table4 shows some inorganic precipitating agents for cations

Table4 : some inorganic precipitating agents for cations.

Weight form	Precipitating agent	Precipitating agent	Ions
$BaCrO_4$	$BaCrO_4$	$(NH_4)_2CrO_4$	Ba^{+2}
$PbSO_4$	$PbSO_4$	H_2SO_4	Pb^{+2}
$AgCl$	$AgCl$	HCl	Ag^{+}
Hg_2Cl_2	Hg_2Cl_2	HCl	Hg_2^{+2}
HgS	HgS	H_2S	Hg^{+2}
Al_2O_3	$Al(OH)_3$	NH_3	Al^{+3}
BeO	$Be(OH)_2$	NH_3	Be^{+2}
$Be_2P_2O_7$	NH_4BePO_4	$(NH_4)_2HPO_4$	Be^{+2}
Fe_2O_3	$Fe(OH)_3$	NH_3	Fe^{+3}
$CaCO_3$ or CaO	CaC_2O_4	$(NH_4)_2C_2O_4$	Ca^{+2}
Sb_2S_3	Sb_2S_3	H_2S	Sb^{+3}
As_2S_3	As_2S_3	H_2S	As^{+3}
$SrSO_4$	$SrSO_4$	H_2SO_4	Sr^{+2}
$Mg_2P_2O_7$	NH_4MgPO_4	$(NH_4)_2HPO_4$	Mg^{+2}
$Zn_2P_2O_7$	NH_4ZnPO_4	$(NH_4)_2HPO_4$	Zn^{+2}

Table5 : some inorganic precipitating agents for anions.

Weight form	Precipitating agent	Precipitating agent	Ions
$AgCN$	$AgCN$	$AgNO_3$	CN^{-1}
AgI	AgI	$AgNO_3$	I^{-1}
$AgBr$	$AgBr$	$AgNO_3$	Br^{-1}
$AgCl$	$AgCl$	$AgNO_3$	Cl^{-1}

AgCl	AgCl	$FeSO_4$ ass. ag./$AgNO_3$	ClO_3^{-1}
CuSCN	CuSCN	SO_2 ass.ag. /$CuSO_4$	SCN^{-1}
$BaSO_4$	$BaSO_4$	$BaCl_2$	SO_4^{-2}

The differences between organic precipiting 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.

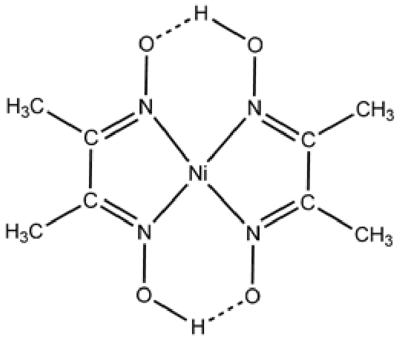
4- Organic precipitating agents give highly colored products, which are easy to detect by colorimetric analysis.

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 $[Fe(SCN)_6]^{3-}$ and $[Fe(SCN)]^{2+}$ .Nitrite ion can be detected from the formation of brown ferrous complex $[Fe(SCN)_6]^{3-}$. Copper as a blue ammonia complex $[Cu(NH_3)_4]^{2+}$.

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 Ni(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.

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