College of science for women
Department of Chemistry

Second Stage

Gravimetric Analysis

Teacher Name:
Dr.Muna Mahmood

Precipitating Agents

Precipitating Agents :Ideally a gravimetric precipitating agent should react specifically or at least selectively with the analyte. Specific reagents which are rare, react only with a single chemical species. Selective reagents which are more common, react with a limited number of species. In addition to specificity and selectivity, the ideal precipitating reagent would react with analyte to give a precipitate that has the preferred requirements which have been previously discussed.

Inorganic precipitating agents :

The inorganic precipitants e.g. S^{2-} , CO_3^{2-} , PO_4^{3-} …etc are usually not selective compared to the organic precipitants but it give precipitates with well known formula .

Some Inorganic Precipitating Agents

Precipitating Agent	Element Precipitated*
$NH_3(aq)$	**Be** (BeO), **Al** (Al_2O_3), **Sc** (Sc_2O_3), Cr (Cr_2O_3)†, **Fe** (Fe_2O_3), Ga (Ga_2O_3), Zr (ZrO_2), **In** (In_2O_3), Sn (SnO_2), U (U_3O_8)
H_2S	Cu (CuO)†, **Zn** (ZnO or $ZnSO_4$), **Ge** (GeO_2), As (As_2O_3 or As_2O_5), Mo (MoO_3), Sn (SnO_2)†, Sb (Sb_2O_3), or Sb_2O_5), Bi (Bi_2S_3)
$(NH_4)_2S$	Hg (HgS), Co (Co_3O_4)
$(NH_4)_2HPO_4$	**Mg** ($Mg_2P_2O_7$), Al ($AlPO_4$), Mn ($Mn_2P_2O_7$), Zn ($Zn_2P_2O_7$), Zr ($Zr_2P_2O_7$), Cd ($Cd_2P_2O_7$), Bi ($BiPO_4$)
H_2SO_4	Li, Mn, **Sr**, **Cd**, **Pb**, **Ba** (all as sulfates)
H_2PtCl_6	K (K_2PtCl_6 or Pt), Rb (Rb_2PtCl_6), Cs (Cs_2PtCl_6)
$H_2C_2O_4$	Ca (CaO), Sr (SrO), **Th** (ThO_2)
$(NH_4)_2MoO_4$	Cd ($CdMoO_4$)†, Pb ($PbMoO_4$)
HCl	**Ag** ($AgCl$), Hg (Hg_2Cl_2), Na (as NaCl from butyl alcohol), Si (SiO_2)
$AgNO_3$	**Cl** ($AgCl$), Br ($AgBr$), I(AgI)
$(NH_4)_2CO_3$	**Bi** (Bi_2O_3)
NH_4SCN	Cu [$Cu_2(SCN)_2$]
$NaHCO_3$	Ru, Os, Ir (precipitated as hydrous oxides, reduced with H_2 to metallic state)
HNO_3	Sn (SnO_2)
H_5IO_6	Hg [$Hg_5(IO_6)_2$]
NaCl, $Pb(NO_3)_2$	F ($PbClF$)
$BaCl_2$	**SO_4^{2-}** ($BaSO_4$)
$MgCl_2$, NH_4Cl	PO_4^{3-} ($Mg_2P_2O_7$)

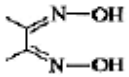
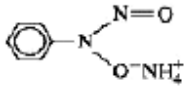
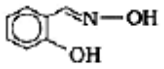
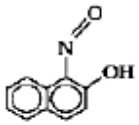
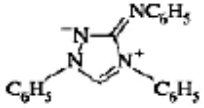
* These reagents typically form slightly soluble salts or hydrous oxides with the analyte. As you can see from the many entries for each reagent, few inorganic reagents are selective.

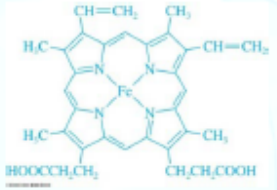
- **Organic precipitating agents** :
- The organic precipitants such as dimethglyoxime and 8-hydroxyquinoline are more selective than inorganic precipitants . They produce with the analyte less soluble precipitate (small Ksp) . They also have high molecular weight so that the weighing error is redued . The disadvantage of organic precipitants is that they usually form with the analyte a precipitate of unknown formula , therefore the precipitate is burned to the metal oxide .

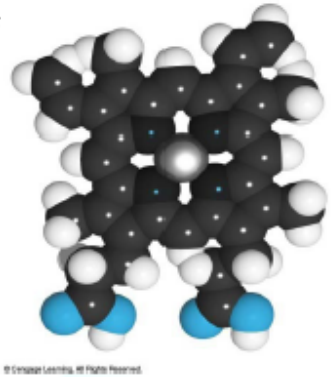
12C-3 Organic Precipitating Agents

- ✓Some organic reagents react with metal ions then produce insoluble coordination cmpds.
- ✓ Reagents that form coordination compounds of this type are called **chelating agents**, and their products are called **chelates**.
- ✓ Those metal chelates are relatively nonpolar and have **low solubilities in water**.
- ✓ Usually, these compounds possess low densities and are often intensely colored. Because they are not wetted by water, coordination compounds are easily freed of moisture at low temperatures.

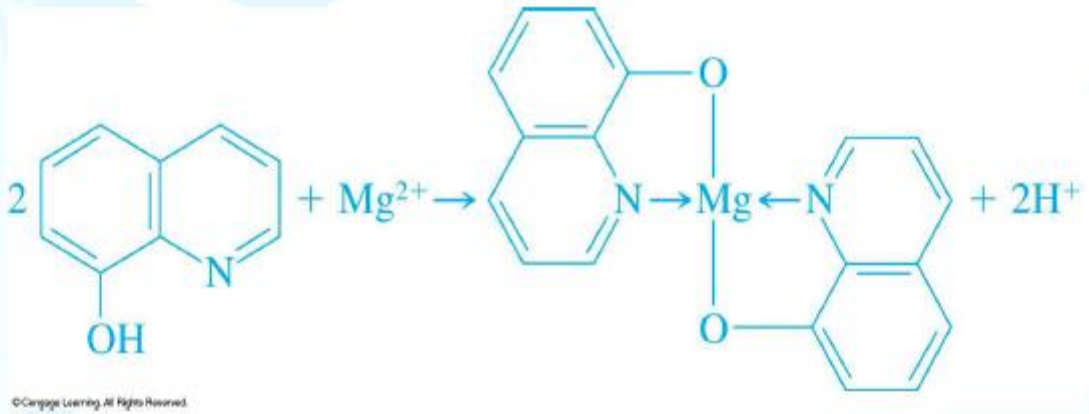
Common organic precipitating agents

Name	Structure	Ions precipitated
Dimethylglyoxime		Ni^{2+}, Pd^{2+}, Pt^{2+}
Cupferron		Fe^{3+}, VO_2^+, Ti^{4+}, Zr^{4+}, Ce^{4+}, Ga^{3+}, Sn^{4+}
8-Hydroxyquinoline (oxine)		Mg^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Fe^{3+}, Bi^{3+}, Ga^{3+}, Th^{4+}, Zr^{4+}, UO_2^{2+}, TiO^{2+}
Salicylaldoxime		Cu^{2+}, Pb^{2+}, Bi^{3+}, Zn^{2+}, Ni^{2+}, Pd^{2+}
1-Nitroso-2-naphthol		Co^{2+}, Fe^{3+}, Pd^{2+}, Zr^{4+}
Nitron		NO_3^-, ClO_4^-, BF_4^-, WO_4^{2-}
Sodium tetraphenylborate	$Na^+B(C_6H_5)_4^-$	K^+, Rb^+, Cs^+, NH_4^+, Ag^+, organic ammonium ions
Tetraphenylarsonium chloride	$(C_6H_5)_4As^+Cl^-$	$Cr_2O_7^{2-}$, MnO_4^-, ReO_4^-, MoO_4^{2-}, WO_4^{2-}, ClO_4^-, I_3^-





Magnesium complex with 8-hydroxyquinoline.



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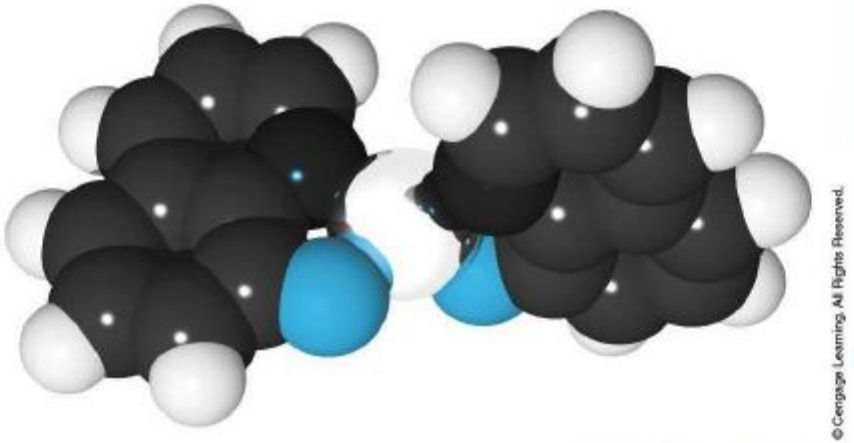

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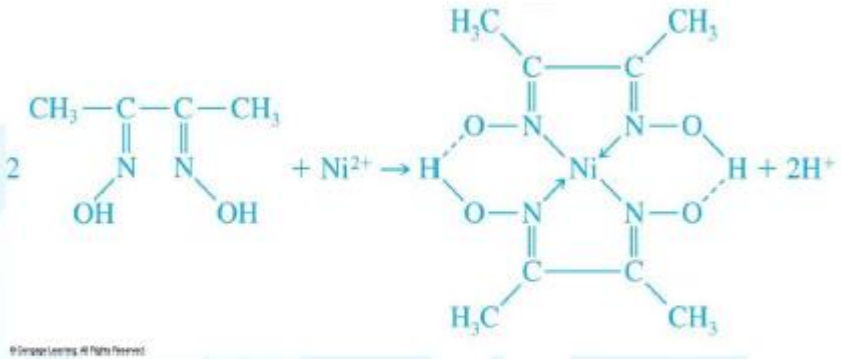
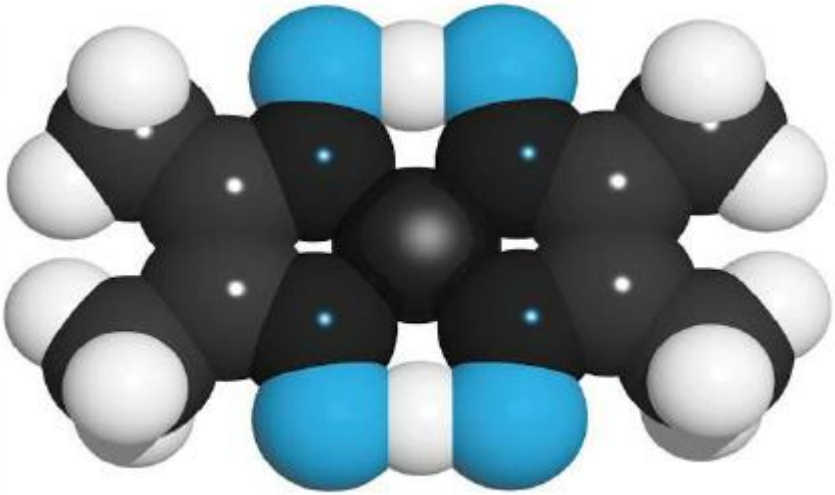


Nickel dimethylglyoxime is spectacular in appearance. As shown in color plate 7, it has a beautiful vivid red color.



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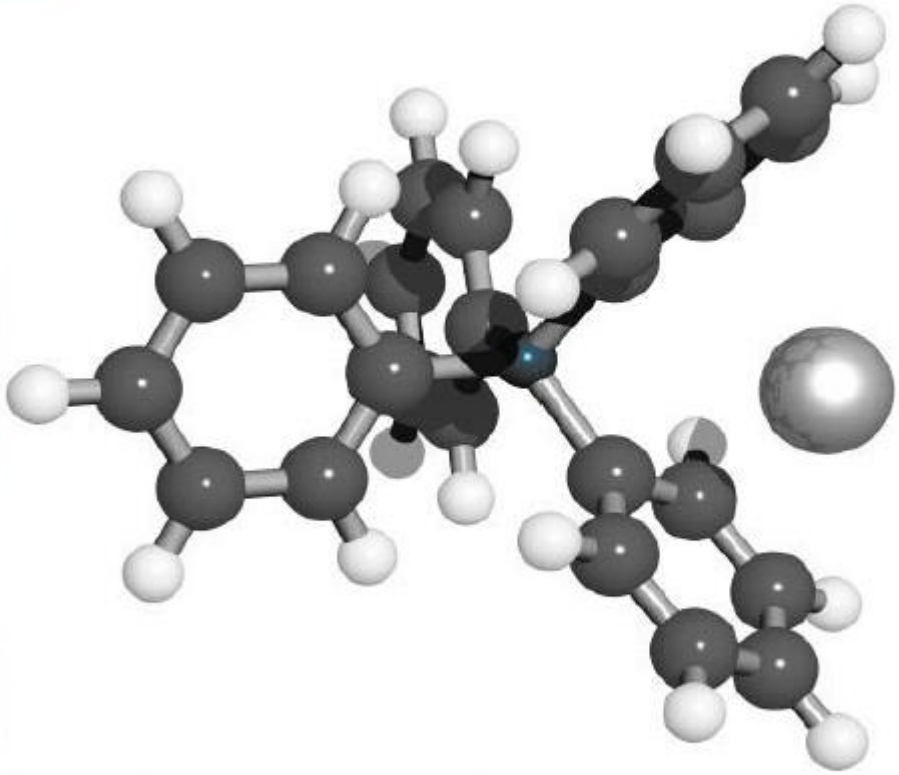
sodium tetraphenylborate.



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12C-4 Organic Functional Group Analysis

- Several reagents react selectively with certain organic functional groups and thus can be used for the determination of most compounds containing these groups.
- Many of the reactions shown can also be used for volumetric and spectrophotometric

TABLE 12-4

Gravimetric Methods for Organic Functional Groups

Functional Group	Basis for Method	Reaction and Product Weighed*
Carbonyl	Mass of precipitate with 2,4-dinitrophenylhydrazine	$RCHO + H_2NNHC_6H_3(NO_2)_2 \rightarrow$ $\underline{R{-}CH{=}NNHC_6H_3(NO_2)_2(s)} + H_2O$ (RCOR′ reacts similarly)
Aromatic carbonyl	Mass of CO_2 formed at 230°C in quinoline; CO_2 distilled, absorbed, and weighed	$ArCHO \xrightarrow[CuCO_3]{230^\circ C} Ar + \underline{CO_2(g)}$
Methoxyl and ethoxyl	Mass of AgI formed after distillation and decomposition of CH_3I or C_2H_5I	$ROCH_3 + HI \rightarrow ROH + CH_3I$ $RCOOH_3 + HI \rightarrow RCOOH + CH_3I$ $ROC_2H_5 + HI \rightarrow ROH + C_2H_5I$ $CH_3I + Ag^+ + H_2O \rightarrow \underline{AgI(s)} + CH_3OH$
Aromatic nitro	Mass loss of Sn	$RNO_2 + \frac{3}{2}Sn(s) + 6H^+ \rightarrow RNH_2 + \frac{3}{2}Sn^{4+} + 2H_2O$
Azo	Mass loss of Cu	$RN{=}NR' + 2Cu(s) + 4H^+ \rightarrow RNH_2 + R'NH_2 + 2Cu^{2+}$
Phosphate	Mass of Ba salt	$ROP(OH)_2 + Ba^{2+} \rightarrow \underline{ROPO_2Ba(s)} + 2H^+$
Sulfamic acid	Mass of $BaSO_4$ after oxidation with HNO_2	$RNHSO_3H + HNO_2 + Ba^{2+} \rightarrow ROH + BaSO_4(s) + N_2 + 2H^+$
Sulfinic acid	Mass of Fe_2O_3 after ignition of Fe(III) sulfinate	$3ROSOH + Fe^{3+} \rightarrow (ROSO)_3Fe(s) + 3H^+$ $(ROSO)_3Fe \xrightarrow{O_2} CO_2 + H_2O + SO_2 + \underline{Fe_2O_3(s)}$

*The substance weighed is underlined.

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- **Organic ppting agents have the advantages**
- 1- Som of organic ppting agents are very selsctive and very broad in the number of elements they will ppt.
- 2- Giving pptes with very low solubility in water
- 3- Give a favorable gravimetric factor